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LVIII. *Further Studies on the Electron Theory of Solids.
The Compressibilities of a Divalent Metal and of the
Diamond. Electric and Thermal Conductivities of Metals.*
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IN a paper published in the Philosophical Magazine, April 1922, I calculated on the Electron Theory of Solids the compressibility of monovalent and trivalent elements crystallizing in the regular system. In this paper I propose to do the same for a divalent element. The simplest case is that of calcium, for Hull has shown that it crystallizes in the regular system and that the atoms are arranged in face-centred cubes. Thus, as far as the atoms are concerned, the metal may be supposed to be built up of cubical units, each unit having $\frac{1}{8}$ of an atom at each corner and $\frac{1}{2}$ of an atom at the centre of each of its six faces. Thus each unit contains four atoms; and as calcium is a divalent element, there must be twice as many disposable electrons in the unit as there are atoms, so that each unit must contain 8 electrons.

A symmetrical way of arranging these 8 electrons is to put $\frac{1}{4}$ of an electron at the middle point of each side of the unit cube, one electron at the centre of this cube, and one electron at the centres of 4 out of the 8 small cubes into which the unit cube is divided by planes bisecting its sides at right angles. These 4 cubes are chosen so that if we

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move parallel to any side of the unit cube, the empty cubes and those containing electrons occur alternately.

Assuming this to be the constitution of the metal, we can easily calculate the electrostatic potential energy by the method given in the paper referred to. Let E be the charge on the calcium atom, e the charge on an electron, and $2d$ the side of the cube taken as the unit. Then the electrostatic potential energy for a single atom is

$$\frac{1}{2}E \left(-\sum \frac{E}{r} + \sum \frac{e}{r'} \right),$$

where r is the distance of an atom and r' that of an electron from an atom under consideration.

The potential energy of an electron is

$$\frac{e}{2} \left(\sum \frac{E}{r'} - \sum \frac{e}{r''} \right),$$

where r'' is the distance of an electron from the one under consideration.

By the method described in the former paper, I find for the electrostatic potential energy of an atom the expression

$$\frac{1}{2}E \left(-E \cdot \frac{16.23}{d} + e \cdot \frac{36.85}{d} \right),$$

which, since $E=2e$, is equal to

$$\frac{e^2}{d} 4.4.$$

The potential energy of a single electron, if it is one at the middle point of a side of the unit cube or at its centre, I find to be

$$\frac{1}{2}e \left(E \cdot \frac{17.97}{d} - e \cdot \frac{35.1}{d} \right) = \frac{1}{2} \frac{e^2}{d} .83,$$

while if the electron is one of those at the centre of the small cubes, the potential energy is

$$\frac{1}{2}e \left(E \cdot \frac{18.87}{d} - e \cdot \frac{35.1}{d} \right) = \frac{1}{2} \frac{e^2}{d} 2.65.$$

Since the neutral calcium atom consists of one positive nucleus and two electrons, one of each type, the potential energy per normal atom will be

$$\frac{e^2}{d} (4.4 + 1.325 + .415) = \frac{e^2}{d} 6.15.$$

If Δ is the density of calcium, M the mass of an atom, since our unit cube with side $2d$ contains 4 atoms,

$$\frac{4M}{8d^3} = \Delta,$$

$$\frac{1}{d} = 2^{1/3} \left(\frac{\Delta}{M} \right)^{1/3}.$$

Hence the electrostatic potential energy per normal atom is

$$e^2 \cdot 6 \cdot 15 \cdot 2^{1/3} \left(\frac{\Delta}{M} \right)^{1/3},$$

and the electrostatic potential energy per unit volume is

$$e^2 \cdot 6 \cdot 15 \cdot 2^{1/3} \left(\frac{\Delta}{M} \right)^{4/3}$$

$$= e^2 \cdot 7 \cdot 75 \times \left(\frac{\Delta}{M} \right)^{4/3}.$$

Hence, by page 736 of the former paper, k the bulk modulus for calcium will be given by

$$k = e^2 \cdot \frac{7 \cdot 75}{9} \left(\frac{\Delta}{M} \right)^{4/3}.$$

For calcium $\Delta = 1 \cdot 85$,

$$M = 40 \times 1 \cdot 64 \times 10^{-24}.$$

This makes $1/k$ the compressibility equal to

$$5 \cdot 9 \times 10^{-13};$$

the value found by Richards is $5 \cdot 5 \times 10^{-12}$, so that the agreement between the calculated and observed values is again quite close. The other divalent metals Mg, Zn, Cd crystallize in the hexagonal system; in this system the elastic properties vary in different directions, and a uniform pressure would produce a change in shape as well as in volume. The arrangement of electrons and atoms appropriate to this case is when the electrons are at the corners of a hexagonal prism and the atom at the centre. To fix the shape and size of the prism we require two lengths, the radius of the base and the height of the prism instead of the one which sufficed for crystals in the regular system. The necessity for taking two variables instead of one makes the calculations more lengthy than those for the regular system, and I shall defer their consideration for the present.

Compressibility of the Diamond.

In the diamond we have a quadrivalent element crystallizing in the regular system. The arrangement of the carbon atom in the diamond has been shown by Sir W. H. Bragg and Professor W. L. Bragg to be given by the following scheme. They occupy

- a*, the corners of a cube ;
- b*, the centres of its faces ;
- c*, 4 of the centres of the 8 cubes into which the large cube is divided by planes bisecting its sides at right angles.

We shall take this cube as our unit ; it contains eight carbon atoms. Since carbon is quadrivalent, it must contain 32 electrons ; these electrons will be situated

- a*, at the middle points of the edges of the cubical unit : this accounts for 3 ;
- b*, at the centres of each of the faces of the 8 small cubes : this accounts for 24 ;
- c*, at the centres of the four small cubes not occupied by the carbon atoms : this accounts for 4 ;
- d*, one at the centre of the large cube.

Making use of this unit, we can calculate the electrostatic potential energy due to the charges on the atoms and electrons. Let E be the charge on a carbon atom, e that on an electron.

The electrostatic potential energy of a carbon atom

$$\frac{1}{2}E \left(\frac{\sum e}{r'} - \frac{\sum E}{r} \right)$$

I find to be equal to

$$\frac{1}{2} \frac{E}{d} (149 \cdot 346 \cdot e - 35 \cdot 13 \cdot E),$$

where $2d$ is the side of a unit cube. Since $E = 4e$, this reduces to

$$17 \cdot 65 \cdot \frac{e^2}{d}.$$

The electrostatic potential energy of an electron I find to be

$$\begin{aligned} & \frac{1}{2} \frac{e}{d} \left\{ \frac{E}{4} \cdot 149 \cdot 346 - 147 \cdot 59 e \right\} \\ &= \frac{1}{2} \frac{e^2}{d} \cdot 1 \cdot 75. \end{aligned}$$

Hence the electrostatic potential energy for the atom and its four associated electrons is $21.15 \frac{e^2}{d}$.

Since there are eight atoms in the cube whose edge is $2d$, if Δ is the density of the diamond and M the mass of a carbon atom,

$$\frac{8M}{8d^3} = \Delta$$

or
$$\frac{1}{d} = \left(\frac{\Delta}{M} \right)^{1/3}.$$

Thus the electrostatic potential energy per one atom and four electrons is

$$21.15 e^2 \left(\frac{\Delta}{M} \right)^{1/3},$$

and the energy per unit volume is

$$21.15 e^2 \left(\frac{\Delta}{M} \right)^{4/3}.$$

Hence, by page 736 of the former paper, k the bulk modulus of the diamond is given by the equation

$$k = \frac{21.15}{9} e^2 \left(\frac{\Delta}{M} \right)^{4/3};$$

for the diamond $\Delta = 3.52$, $M = 12 \times 1.64 \times 10^{-24}$; hence

$$k = 5.6 \times 10^{12}, \quad 1/k = .178 \times 10^{-12}.$$

This value for $1/k$ is much less than that, $.5 \times 10^{-12}$, found by Richards. It is, however, in close agreement with $.16 \times 10^{-12}$, the value recently found by Adams (Washington Acad. Sc. xi. p. 45, 1921).

The properties of solids formed by elements whose atoms have more than four disposable electrons are quite different from those of solids formed by the elements with one, two, or three disposable electrons. The latter are, with the exception of boron, metallic and good conductors of electricity and heat. The former, for instance sulphur and phosphorus, are insulators. Not only do they insulate in the solid state, but they do so after they are fused. They differ in this respect from solid salts which, though they may insulate when in the solid state, generally conduct when melted. This suggests that in the salts there are positively and negatively electrified systems which are fixed when the substance is in the solid state, but can move about when it is liquefied. In such elements as sulphur or phosphorus there does not seem to be any evidence of the existence of

anything but neutral systems ; in other words, the solid may be regarded as built up of units, each of which contains as much positive as negative electricity. It is noteworthy that according to the Electron Theory of Chemical Combination, two similar atoms if they have each more than four disposable electrons, like the atoms of sulphur and phosphorus, can combine and form a saturated molecule, which is electrically neutral.

Thus we are led to distinguish three types of solids :—

- a. A type where the atoms are arranged in lattices, and the electrons in other lattices coordinated with the atomic ones. In this type each electron has no closer connexion with a particular atom than it has with several others. Thus, for example, when the electrons form a simple cubical lattice with the atoms at the centres of the cubes, each electron has 8 atoms as equally near neighbours ; so that an electron is not bound to a particular atom. This type includes the metals ; it also includes boron and carbon in the form of diamond, which are insulators.
- b. A type represented by the salts ; here the atoms are again arranged in lattices, but each electron has much closer relation with one particular atom than it has with any other. Thus to take the case of Na.Cl, where the Braggs have shown the atoms to be arranged according to the following scheme :—

Na	Cl	Na	Cl
Cl	Na	Cl	Na
Na	Cl	Na	Cl

We suppose that each sodium atom has lost an electron, while each chlorine atom has gained one ; thus each chlorine atom has eight electrons around it, and each electron is much more closely bound to one particular chlorine atom than to any other. It is so closely associated that it is not dissociated from its partner in either the solid or liquid state of the substance. Thus the chlorine system always has a negative charge, the sodium one a positive. These atoms do not move when the substance is in a solid state, though they may do so when it is liquefied.

If the distance of the electrons from the chlorine atoms were to increase until it was not far from half the distance between the sodium and chlorine nuclei this type would approximate to type *a*.

- c. A type where the lattices are built up of units which are not electrified ; such units are probably molecules containing two or more atoms, though in certain cases they may be single atoms. The characteristic of the type is that each unit has sufficient electrons bound to it to make it electrically neutral, and that each electron remains attached to a particular atom. Thus where an electric force acts on the system there is no tendency to make the unit move in one direction rather than the opposite, so that the substance cannot conduct electricity.

Metallic Conduction.

We now pass on to consider why it is that the arrangement of atoms and electrons in type *a* is in many cases, though not in all, connected with the property of metallic conduction. The consideration of the frequencies of the vibrations of the electrons in a lattice will, I think, throw light on this connexion. I showed (Phil. Mag. April 1922, p. 721) that these frequencies may extend over a very wide range of values as the type of displacement of the electrons is altered. Thus, if all the electrons in a region whose linear dimensions are large compared with $2d$, the distance between two electrons, have the same displacement relatively to the atoms, the frequency n of the vibrations for the alkali metals is given by the equation

$$mp^2 = \cdot 384c \cdot e^2/d^4. \quad . \quad . \quad . \quad . \quad (1)$$

This frequency, even in the case of the univalent element, corresponds to that of light in the visible part of the spectrum ; for elements of greater valency it is far in the ultra-violet. This is also the frequency with which a single electron vibrates if the surrounding atoms and electrons are fixed. As those frequencies are so great very little energy will go into them at ordinary temperatures, and they will have little or no effect on the specific heat of the solid.

There are, however, other types of vibration for which the periods may be very long. Thus if all the electrons on a certain line of the lattice are displaced along the lattice by the same amount, while those on adjacent lattices are displaced in the opposite direction, the frequency is given by the equation

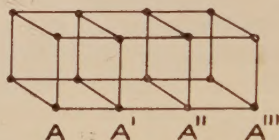
$$mp^2 = \frac{\cdot 384c \cdot e^2}{d^4} - \frac{5 \cdot 2e^2}{d^3}; \quad . \quad . \quad . \quad . \quad (2)$$

thus we see that only under certain conditions is the expression for p^2 positive, and it is only under these that the

equilibrium is stable for this mode of displacement. A negative term will occur in the expression for p^2 if the electrons along one line of the lattice are displaced relatively to those on adjacent lines, even though the displacements are not equal and opposite. The view I wish to put forward is that in metals the frequency of this type of vibration is so low that the equilibrium for such a displacement is practically neutral, and therefore that a system vibrating in this way can absorb at any temperature the full amount of energy which at that temperature corresponds to each degree of freedom.

It may be desirable to illustrate the argument by a particular case (fig. 1). Let us take that where the electrons

Fig. 1.



are arranged in a simple cubical space lattice with the atoms at the centres of the cubes. Then, if an electron were displaced independently of the others, the frequency of its vibration would be very great and it would absorb very little energy; while if a chain of electrons along a lattice like $AA'A''A'''$ were displaced along the line of the lattice, the time of vibration of the chain might be comparatively infinite, so that the chain would absorb the full amount of energy corresponding to one degree of freedom. However many electrons there may be in the chain, it has only one degree of freedom, for the nature of the displacement supposes that they move as a rigid body along a definite line. To sum up, the study of the frequencies of vibrations of the lattice of electrons shows that while at ordinary temperatures little energy could go into vibrations corresponding to the motion of an electron as a separate individual, yet groups of electrons along a lattice forming a rigid chain and moving in the direction of the length of the chain might absorb a full quantum of energy.

Thus in a solid with the constitution we have sketched, chains of electrons lying along a line of a lattice may be travelling along that line carrying energy and electricity from one part of the solid to another; the frequency of

vibrations of these chains is so low that they readily absorb energy even at low temperatures, so that the average energy of the chains at the absolute temperature is $k\theta$, where k represents the factor corresponding to one degree of freedom.

Thus, though the electrons in the solid are not free, and are in a very different condition from those of an electron gas diffused through the solid, yet like those in the gas they can carry energy and electricity from one place to another. In the gas, however, each electron is supposed to be moving independently of its neighbour, and also to possess energy $3k\theta$ corresponding to three degrees of freedom; in our case the agents which carry heat and electricity are not isolated electrons, but chains of electrons moving as if the electrons which compose them were rigidly connected together; thus, however many electrons there may be in the chain, the average energy of a chain will only be $k\theta$, *i. e.* one-third of that of each electron on the gas theory. Thus on this view the contributions of the electrons to the specific heat of the solid will be a very small fraction of the contribution of the same number of electrons on the gas theory.

Professor Lindemann has given (*Phil. Mag.* xxix. p. 127, 1915) a theory of Metallic Conduction which, though on quite different lines to the present one, agrees with it in making the electrons which carry the current move along the lines of the lattices, and in the view that the electrons make no appreciable contribution to the specific heat.

The existence of these chains requires that the frequency of this vibration should be exceedingly small; if the dimensions and arrangements of the lattice are such that the frequencies given by equation (2), are not less than 10^{13} or so, the chains will not absorb energy at moderate temperatures, and at these temperatures the solid will act as an insulator. Thus it requires special conditions for the lattices of electrons to give rise to conductivity, so that the fact that neither boron nor the diamond is a conductor is not inconsistent with the theory. The motion of the chains need not necessarily be a reciprocating motion, for if the amplitude of excursion of an electron in the chain exceeds half the distance between two electrons, an electron such as A' would shoot past another position of equilibrium; the forces acting on it would change sign and would tend to increase the distance still further; thus the chain would continue to move on in one direction and would not oscillate backwards and forwards.

On the Origin of the Chains.

If we consider the state of things inside a solid, we can I think see reasons for believing that the existence of moving chains of electrons is probable. The solid is traversed by the radiation corresponding to the radiation from a black body at the temperature of the solid. This radiation consists of a series of discrete pulses, each pulse being the seat of intense electrical forces. When the effect of these pulses is represented by a Fourier series of waves, the wave-length for which the intensity of the light is a maximum is inversely proportional to the absolute temperature, and at 0° C. is about 10^{-3} cm.

We may suppose that the linear dimensions of the regions occupied by individual pulses are grouped about a mean which varies inversely as the absolute temperature, and which is large compared with the distance between two electrons. Thus the radiation will furnish fields of electric force which have a high and fairly constant value over a length which includes a good many electrons; and the electrons in a lattice will from time to time be exposed to electric forces extending over a considerable length, and thus a chain of electrons will be started in motion as a whole. We should expect the average length of the chain to be inversely proportional to the absolute temperature. Moreover, such chains of electrons moving past the atoms would themselves tend to set up pulses of radiation, the dimensions of the pulse being commensurate with the length of the chain. Thus there would be a kind of regenerative action; the radiation would tend to produce the chains, while the chains would tend to produce the radiation. When the two processes got into equilibrium the radiation would be that corresponding to the black body radiation at the temperature of the solid, while the average kinetic energy of the chains would be proportional to the absolute temperature.

When the solid is not acted upon by electric forces, there will be as many of these chains moving in any one direction as in the two opposite, so that there will be no current of electricity through the solid as a whole. The motion of the chains will give rise to "local currents" whose distribution might be affected by magnetic forces.

We shall now consider the effect of an electric force on the motion of the chains.

On the old theory that the electrons moved freely through the metal and kept striking against its atoms, the result of an electric force X was to give to the electrons an average

velocity in the direction of the electric force equal to $Xe\lambda/2mv$, where λ is the mean free path of an electron and v the mean velocity. This result is obtained as follows: in a collision between an electron and an atom, since the mass of the electron is infinitesimal in comparison with that of the atom, there will be no "persistence" of the velocity of the electron. The velocity communicated by the electric force to the electron before it came into collision with an atom will, as it were, be completely wiped out by the collision, and the electron will make an entirely fresh start. Thus if t be the interval between two collisions, the average velocity of the electron in the direction of the electric force will be

$$\frac{1}{2} \frac{Xe}{m} t, \quad \text{or} \quad \frac{1}{2} \frac{Xe \lambda}{m v}.$$

On the theory we are now discussing, the carriers of electricity are not free electrons, but chains of electrons rigidly connected moving along a line of the lattice; since the chain has only one degree of freedom, the average energy of a chain at the temperature θ is $R\theta/2$; hence

$$\frac{1}{2}nmv^2 = \frac{1}{2}R\theta, \quad \dots \dots \dots (3)$$

where n is the number of electrons in the chain and v its velocity. Thus the average energy of a single electron in the chain is $R\theta/2n$. On the old theory when each electron was supposed to be free, its average energy was $3R\theta/2$. The energy and velocity of an electron on the new theory are smaller than on the old.

The "collisions" between the electrons and atoms are also different. On the new theory an electron in a chain is moving past a row of atoms arranged at equal intervals $2c$ along a line parallel to the path of an electron; the time it takes for an electron to pass from closest proximity to one atom to closest proximity to the next is $2c/v$. If the interchange of energy between the electron and the atom were limited to the time when the electron was closest to the atom, the electron for a time $2c/v$ would not be losing any energy, and so could, under the electric force, acquire a velocity equal to $Xe \cdot 2c/mv$. The loss of energy by the electrons will not, however, be confined to the positions of closest proximity, but will extend some way on either side. The result of this will be that in part of the interval $2c/v$ the electron will be losing velocity, so that the velocity it will acquire under the electric force will be less than $Xe \cdot 2c/mv$, and the average velocity will be less than half this value.

We shall suppose that the average velocity due to the electric force is

$$g \frac{Xe}{m} \frac{c}{v}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where g is a fraction. This by equation (3) is equal to

$$g \frac{Xencv}{R\theta} = g \frac{eXlv}{2R\theta},$$

where l is the length of the chain.

If q is the number of chains parallel to x per unit volume, the number crossing unit area in unit line is equal to

$$g \frac{Xe}{2R\theta} \cdot q;$$

and since each chain carries ne units of electricity, the current across unit area is

$$g \frac{Xe^2nlv}{2R\theta} q.$$

Hence σ , the specific electrical conductivity, is given by the equation

$$\sigma = g \frac{e^2lvnq}{2R\theta} = g \frac{e^2lvfp}{2R\theta}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where p is the number of electrons per unit volume and f the fraction of them formed into chains.

On the theory we are considering, these moving chains are responsible not only for the electrical conductivity of metals, but also for the production and absorption of the radiation which fills the space occupied by the metal. They may be regarded as in some ways analogous to Planck's oscillators, the slowly moving ones corresponding to oscillators with a long period of vibration, producing mainly the long wave radiation while the chains with high velocities give out the radiation corresponding to the shorter wave-lengths. We see from equation (3) that, at the same temperature, the chains which have a high velocity contain a small number of electrons and are therefore short, the chains which have a small velocity contain a large number of electrons and are long. Thus the long chains produce the long wave-length radiation, the short chains the short waves. We should expect on this view that the lengths of the various chains in a metal should be distributed according to a law analogous to that which governs the distribution of the energy corresponding to waves of different wave-lengths in the radiation from a black body. But according to Wien's Displacement Law, the length-scale of the radiation varies inversely as the absolute temperature; $\lambda_m\theta = \text{a constant}$. Hence we conclude

that the average number of electrons in a chain varies inversely as the absolute temperature.

If $cn = \beta/\theta$, where β is a constant, then by equation (3)

$$v = \left(\frac{Rc}{\beta m} \right)^{\frac{1}{2}} \theta.$$

Thus ncv is independent of the temperature except for the variation in c , due to the alteration in the volume of the metal caused by a change of temperature. p , the number of electrons per unit volume, will only change with the temperature through thermal expansion. Hence we see from the expression (5) for the conductivity that if the number of electrons concerned in carrying the current does not vary with the temperature, the specific conductivity will vary inversely as the absolute temperature, which is very approximately true for pure metals.

Resistance under rapidly Alternating Forces.

We can get an estimate of the average velocity of the chains in the following way:—In the preceding investigation we have supposed that the electric force acting on the metal was steady. The argument will evidently not hold when the force is alternating so rapidly that while the electron is passing through the distance $2gc$ the force changes its direction; for in that case the effect of the electric field in altering the motion of the chains will be much less than that expressed by equation (4). When the force is reversed many times during this period there will be very little alteration, and therefore very little conductivity. Thus the resistance of metals under alternating forces should begin to increase when the period of alternation becomes comparable with the time taken by an electron in a chain to travel over a distance equal to g times that between two electrons in the chain. When the period of alternation is considerably greater than this time we should not expect the resistance to vary with the period.

Rubens and Hagen determined the conductivity of metals under alternating forces by measuring the amount of light of very long wave-length reflected from the surface of the metals. They found that the electrical conductivity of certain metals at room temperature under electrical waves whose wave-length was 2.5×10^{-3} cm. was the same as the conductivity under steady electrical forces, and that even when the wave-length was as short as 4×10^{-4} cm. the electrical conductivity was within about 20 per cent. of that

for steady forces. As the period of the longer waves is 8.3×10^{-14} second, we may conclude that the time taken for an electron in a chain to pass over g times the distance which separates it from its next neighbour in the chain cannot be greater than about 10^{-13} second. If we take the distance between 2 electrons as 2×10^{-8} , this would make the minimum velocity of the chains about $2g \times 10^5$. This refers to the temperature at which Rubens and Hagen made their experiments—presumably about 15°C . As the velocity of the chains decreases as the temperature falls, the reflexion from a metallic surface should become at very low temperatures abnormal at longer wave-lengths than those determined by Rubens and Hagen.

We can get in another way an estimate of the magnitude of the time taken by an electron in a chain to pass over a distance equal to half the distance between two neighbouring electrons in the chain. At the temperature of 15°C . the wave-length of the light of maximum intensity in the black body radiation is 10^{-3} cm.; the time of vibration of this light is $\frac{1}{3} \times 10^{-13}$ sec. We should expect from the way we have supposed the black body radiation to arise, that this time would be of the same order as that taken on the average by an electron in the chain to pass over g times the distance between two electrons, and so again we arrive at 10^{-13} sec., as being a time of this order.

On the supposition that c/v is proportional to the time of vibration of the light of greatest intensity, we have

$$\frac{c}{v} = \frac{\gamma}{\theta},$$

where γ is a constant which does not depend on the metal.

$$\text{Hence} \quad ncv = \frac{nv^2\gamma}{\theta},$$

$$\text{but} \quad \frac{1}{2}mnv^2 = \frac{1}{2}R\theta,$$

m being the mass of an electron ; thus

$$nv^2 = \frac{R}{m}\theta = 1.51 \times 10^{11} \times \theta.$$

$$\text{Thus} \quad ncv = 1.51 \cdot \gamma \times 10^{11}.$$

The specific conductivity

$$\begin{aligned} &= gfn \frac{e^2ncv}{R\theta} \\ &= \frac{1.51 \times 10^{11} \gamma g f p e^2}{R\theta}; \end{aligned}$$

in this expression the only factor which varies from one metal to another is fp , the number of electrons made up into chains; the conductivities of metals at the same temperature are directly proportional to the number of electrons in unit volume which take part in carrying the current.

We can put the expression for the conductivity in the form

$$gfp \frac{e^2 c}{m v}.$$

If we take gc/v at 15°C. to be 10^{-13} , since

$$e^2/m = 2.8 \times 10^{-13},$$

the conductivity at this temperature is equal to

$$fp \times 2.8 \times 10^{-26}.$$

The values of f calculated from this expression for some metals are given in Table I.

TABLE I.

Metal.	Conductivity at 15° .	p .	f .
Lithium	1.1×10^{-4}	$.25 \times 10^{23}$.16
Sodium	2.0 "	.15 "	.47
Potassium	1.4 "	.07 "	.70
Rubidium83 "	.06 "	.50
Cæsium5 "	.048 "	.35
Calcium	1.3 "	.25 "	.19
Magnesium	2.3 "	.48 "	.17
Zinc	1.65 "	.75 "	.08
Cadmium	1.3 "	.50 "	.09
Aluminium	3.3 "	1.0 "	.12

Thus on this theory, potassium has a much larger percentage of its electrons moving about in chains than any other metal.

To form an estimate of the average number of electrons in a chain and the velocities of the chains, we may proceed as follows:—If we suppose that at 15°C. , $gc/v = 10^{-13}$, then if $c = 10^{-8}$, which is about right for sodium, $v = 10^5 \times g$. When v is known, we can get n from the equation

$$\frac{1}{2} mnv^2 = \frac{1}{2} R\theta.$$

If $v = 10^5 g$, this equation gives

$$n = 4.4 \times 10^3 / g^2.$$

As g must be less than unity, the chains at this temperature

will on the average probably contain more than 10,000 electrons, and their average length would be greater than $2 \cdot 10^{-4}$ cm. As the average length of the chains varies inversely as the temperature, the average length at 3° Ab. would be greater than $\cdot 02$ cm. and their average velocity less than 10^3 cm./sec.

Super-Conductivity.

The expression for the specific conductivity given by equation (5) is based on the assumption that in a "collision" between an electron and an atom, the energy imparted to the electron by the electric field is given up to the atom during this "collision," so that the electron starts as it were afresh after each collision. For this to happen there must during the collision be a considerable transference of energy from the electron to the atom. The energy of the atoms is due to their vibrations about positions of equilibrium, and the frequencies of these vibrations, according to the experiments of Nernst and Lindemann on the variation of the specific heats with temperature, range from 10^{12} to 10^{13} for the different metals. Now, it follows from general dynamical principles that a collision lasting for a time which is long compared with the time of vibration of a system, will excite very little vibration in the system and communicate very little energy to it. The amount of energy communicated will fall off very rapidly as the ratio of the duration of the collision to the time of vibration increases. In a case considered by Jeans, 'Kinetic Theory of Gases,' § 481, the energy communicated to the system was proportional to e^{-2cp} , where c is the duration of the collision and p the frequency of the free vibration of the system. It follows from this that when the chains of electrons are moving so slowly that the time of a collision is long compared with the time of vibration of the atom, very little energy will be transferred. Our expression for the electrical conductivity was, however, obtained on the assumption that at each collision the excess energy due to the electric field was given up. If, however, the transference of energy is not sufficient to allow of this, the average velocity of the electrons will be greater than that calculated, and the conductivity greater to a corresponding extent. If there were no transference of energy, the average velocity of the electrons and the electrical conductivity would both be infinite. We see then that when the temperature gets so low that the time taken by an

electron to pass over a distance $2c$ is comparable with the time of vibration of the atom, any diminution in the temperature will produce an abnormally large increase in the conductivity, and thus the metal would show the super-conductivity discovered by Kammerlingh-Onnes.

The numbers we have just obtained for sodium show that at a temperature of 3° Ab. the time taken by a collision would be greater than 2×10^{-11} , and this is very long compared with the time of vibration of the sodium atoms, which have a frequency of 3.96×10^{12} . There would be very little transference of energy at this or even considerably higher temperatures, so that the conductivity would be very great.

We have associated the time taken by a chain to pass over the distance $2c$ at any temperature with the time of vibration of the light of predominant energy at that temperature. On the theories of the variation of specific heat with temperatures given by Nernst, Einstein, and Debye, this variation is a function of the ratio of the time of vibration of this light to the time of vibration of the atom. Thus on the view that the average time of a collision is about that of the time of vibration of this light, the variation of the specific heat with temperature and the communication of energy from the electron to the atom depend upon exactly the same quantity, and thus the variation of the specific heat with temperature ought to be closely connected with the super-electrical conductivity. The product $\theta\sigma$ of the temperature and the electrical conductivity ought to change rapidly with the temperature when the specific heat does so. The product $\theta\sigma$ will increase as the specific heat diminishes; if, however, we were to plot the reciprocal of $\theta\sigma$ against the temperature, we should expect to get a graph very similar to the one representing the connexion between specific heat and temperature.

That a connexion of this kind does exist between $1/\theta\sigma$ and the specific heat is, I think, shown by Table II., which contains the values of $1/\theta\sigma$ for lead and silver calculated from the values of the resistances given by Kammerlingh-Onnes (communications from the Physical Laboratory of Leiden, cxix. 1911); the third column contains the values of θ/Θ when $\Theta = h\nu/R$, where N is the time of vibration of the atom; the fourth column gives the value of the specific heat calculated by Debye's theory (Jeans, 'Kinetic Theory of Gases,' §§ 553); and the fifth column the ratio of $1/\theta\sigma$ to the specific heat.

TABLE II.

Lead, $\Theta = 95$.

θ .	$1/\theta\sigma$.	θ/Θ .	Specific heat.	Ratio of $1/\theta\sigma$ to specific heat.
273	366	2.88	.993	368
169.3	351	1.78	.984	357
77.9	325	.82	.928	350
20.18	150	.215	.41	365
13.88	87	.145	.2	435

Silver, $\Theta = 215$.

273	366	1.27	.965	380
169.3	343	.79	.924	373
77.9	252	.362	.691	365
20.18	45	.095	.073	615

Thus except at the lowest temperatures the ratio of $1/\theta\sigma$ to the specific heat is fairly constant; and inasmuch as Kammerlingh-Onnes and Clay have shown that when a small amount of impurity is present, the resistance at very low temperatures approaches a finite value instead of continually diminishing as the temperature falls, it is evident that at these temperatures a trace of impurity would produce a large increase in the value of $1/\theta\sigma$. The higher the value of Θ , the higher will be the temperature at which an abnormally large increase of the conductivity with fall of temperature sets in. Of all metals, beryllium has the smallest atomic value, and so we should expect it to have the greatest value of ν and Θ ; it seems probable that the temperature coefficient of this metal may be abnormal even at room temperatures.

Thermal Conductivity.

The motion of the chains of electrons along the lines of the lattices will in an unequally heated conductor tend to equalize the temperature, for much the same reason as on the Kinetic Theory of Gases the conduction of heat is brought about by the motion of the molecules of a gas. There are, however, several points of difference which require discussion before we can proceed to find an expression for the thermal conductivity on the chain electron theory. When the temperature is uniform, there is no ambiguity in the statement that the average kinetic energy of the chain is that corresponding to one degree of freedom. A chain of electrons, however, stretches over a distance large compared with the distance between two atoms, and when the temperature is not uniform the temperature at one end of the chain may not be the same as that at the other. As the

electrons in the chain move like a rigid body, each electron has the same kinetic energy; we shall suppose that this energy is the same as if the whole of the chain were at the temperature of its middle point, so that the kinetic energy of the whole chain is that corresponding to one degree of freedom at the temperature of the middle point of the chain.

Another important point is that the energy carried across a plane by a chain of electrons passing right across it may, when the temperature is not uniform, be much greater than the actual kinetic energy in the chain when it first reaches the plane. This is important because if it were not so the transport of energy due to the motion of the chains would not be great enough to account for the observed thermal conductivity even if every disposable electron were utilized to make up the chain. It must be remembered that on this theory the number of disposable electrons in unit volume is known; for example, in the alkali metals it is equal to the number of atoms, and cannot be regarded as a quantity which can be adjusted so as to give the right value to the thermal conductivity.

To see how this additional transport of energy is brought about, consider what happens when a chain of electrons ABCDE crosses the plane ZZ, moving past the atoms in its neighbourhood and exchanging energy with them. If $2c$ be the distance between neighbouring electrons or atoms, we shall define a collision between an atom and an electron to be the passage of an electron past its shortest distance from the atom. If we take the axis of x parallel to the chain, then when the head A of the chain reaches ZZ each of the electrons in the chain has $1/n$ of the energy corresponding to one degree of freedom at the temperature $\theta + \frac{l}{2} \frac{d\theta}{dx}$, where l is the length of the chain, n the number of its electrons, and θ the temperature of the plane ZZ. When A makes a collision with the atoms just to the left of the plane ZZ, it will momentarily lose an amount of energy proportional to $\frac{1}{2} \frac{l}{n} \frac{d\theta}{dx}$. This will lower its energy below that which must be possessed by every electron in a chain whose middle point is now at a place where the temperature is $\theta + \frac{1}{2}(l-2c) \frac{d\theta}{dx}$; this energy only differs from that before impact by $\frac{2c}{2n} \frac{d\theta}{dx}$; the electron has, however, since l is much

greater than $2c$, lost far more than this, so that energy must be transmitted along the chain to A to bring its energy up to its proper value. Thus when the electrons are connected together in chains, the transference of energy is not confined to the energy carried by the electrons when they are crossing the plane; each collision made by an electron in the chain will, until the whole of the chain has passed the plane, result in the transference of energy across the plane; if the chain is long this second type of transference may far exceed in magnitude that which would occur if there were no collisions.

We shall now proceed to find an estimate of the transference due to the collisions.

Let us take the electrons in the chain in pairs, the constituents of a pair being equally distant from the centre; let this distance be y . Then, as the chain moves along, one of the constituents of the pair has energy corresponding to a temperature $y \frac{d\theta}{dx}$ above, the other constituent the energy corresponding to the temperature $y \frac{d\theta}{dx}$ below the temperature of its position. If $\frac{1}{2}R\theta$ is the energy corresponding to one degree of freedom at the temperature θ , this excess or defect of energy of an electron will be $\frac{1}{2} \frac{y}{n} R \frac{d\theta}{dx}$. We shall suppose that at each collision of an electron with an atom the energy of the electron is restored to the value corresponding to its position.

Let us begin with the electrons at the beginning and end of the chain. We have seen that the first collision of the front electron after passing the plane results in the transference of $\frac{Rl}{4n} \frac{d\theta}{dx}$ units of energy across the plane. The collision made by the electron in the rear will result in its gaining $\frac{Rl}{4n} \frac{d\theta}{dx}$ units of energy; this will have to be given up by the chain, but inasmuch as all the chain is on the right of the plane ZZ , the energy will be given off in this region and will not be transferred across the plane.

Thus the first collision of this pair of electrons transfers

$$\frac{Rl}{4n} \frac{d\theta}{dx}$$

units of energy across the plane.

Let us now consider the next collision. The front electron

will lose $\frac{Rl}{4n} \frac{d\theta}{dx}$ units of energy, and this will have to be supplied from the chain; since part of the chain is now on the left-hand side of the plane, some of this energy will come from this part, and will not be transferred across the plane. The energy coming from the part of the chain to the right will be transferred across the plane; the ratio of the length of chain to the right of the plane to the length of the chain is $(l-2c)/l$. We suppose that this fraction of the whole energy comes from the part of the chain to the right, and so is transferred across the plane. Thus the transference of energy due to the second collision of the front electron is

$$\frac{Rl}{4n} \frac{d\theta}{dx} \cdot \frac{l-2c}{l}.$$

Now consider the second collision of the electron at the rear of the chain.

This electron will by the collision receive $\frac{lR}{4n} \frac{d\theta}{dx}$ units of energy, and as there are a large number of electrons in the chain practically the whole of this must be given out again by the chain. If it is given out uniformly from all parts of the chain, since the length of the portion to the left of the plane ZZ is $2c$, the amount of energy given out in this region, which is the amount transferred across the plane ZZ, is

$$\frac{lR}{4n} \frac{d\theta}{dx} \cdot \frac{2c}{l}.$$

Thus at the second collision of this pair of electrons the energy transferred across the plane is equal to

$$\begin{aligned} \frac{lR}{4n} \frac{d\theta}{dx} \cdot \frac{l-2c}{l} + \frac{lR}{4n} \frac{d\theta}{dx} \cdot \frac{2c}{l} \\ = \frac{lR}{4n} \frac{d\theta}{dx}, \end{aligned}$$

the same as that transferred at the first collision. We can see that this must be true of all the collisions; and as there are n of these before the chain gets right across the plane, the total amount of energy transferred across the plane by the collision of this pair of electrons is equal to

$$\frac{lR}{4} \frac{d\theta}{dx}.$$

For a pair of electrons at a distance y from the centre of the chain, the interchange of energy at each collision with an atom is $\frac{y}{2n} \frac{Rd\theta}{dx}$, and the number of collisions with one

member of the pair in front of the plane is equal to $2ny, l$; hence the energy transferred by this pair is $\frac{y^2 R d\theta}{l dx}$. Thus, giving y all possible values, we find that the total amount of energy transferred across the plane ZZ through the collisions of all the electrons in the chain is

$$\begin{aligned} & \frac{R d\theta}{l dx} \left(\binom{l}{2} + \binom{l-2c}{2} + \binom{l-4c}{2} + \dots \right) \\ &= \frac{nl}{24} \frac{R d\theta}{dx} \text{ when } n \text{ is large.} \end{aligned}$$

Thus if there are q chains per unit volume, and if v is their average velocity, the energy transferred across unit area per second is

$$\frac{nl}{24} qvR \frac{d\theta}{dx}.$$

In making this rough estimate of the transference of energy, we have supposed that the transference occurred only when the electron was in closest proximity to the atom. The process by which the electron first loses energy to the atom and regains it again by a transference of energy along the chain will begin before the electron reaches its shortest distance from the atom and go on after it has passed it; the result of this will be that at each passage of an electron past an atom the transference of energy may be very considerably greater than that in the case we have considered. We must therefore suppose that the transference of energy at each collision is not $\frac{y}{2n} \frac{R d\theta}{dx}$ but a multiple of this, viz.

$$\frac{\epsilon y}{2n} \frac{R d\theta}{dx},$$

where ϵ is a number greater than unity which depends on the law of force between the electron and the atom. This will make the transference of energy across unit area per second equal to

$$\frac{1}{24} \epsilon n l q v R \frac{d\theta}{dx},$$

where q is the number of chains per unit volume and v the velocity of a chain. Hence K , the thermal conductivity of the metal, is given by the equation

$$\begin{aligned} K &= \frac{1}{24} \epsilon n l q v R \\ &= \frac{1}{24} \epsilon j p l v R. \end{aligned}$$

The ratio of K to σ , the electrical conductivity, is given by the equation

$$\frac{K}{\sigma} = \frac{1}{12} \frac{\epsilon}{g} \frac{R^2 \theta}{e^2}.$$

The right-hand side of this equation does not involve any quantity peculiar to the metal; hence the ratio of the thermal to the electrical conductivity should at the same temperature be the same for all metals, and at different temperatures should be proportional to the absolute temperature. This is the well-known law of Wiedemann and Franz, which is obeyed with fair accuracy by many metals.

Summary.

This paper contains a calculation of the compressibility of a divalent element, calcium, and also that of the diamond by the method given in my paper on the Electron Theory of Solids (Phil. Mag. April 1921). The results obtained are in good agreement with those found by experiment. The same theory is then applied to the consideration of metallic conduction, electrical and thermal. It follows from the theory that when an individual electron is displaced relatively to its neighbours, the frequency of the vibration is that corresponding to the visible or ultra-violet part of the spectrum; these vibrations would not, unless at extremely high temperatures, absorb an appreciable amount of energy. When, however, instead of a single electron being displaced, a chain of electrons lying along one of the lines of the lattice is displaced as a rigid body relatively to the neighbouring atoms and electrons, the time of vibration of this chain may be very long, so long that even at very low temperatures the chain may acquire the full quantum of kinetic energy corresponding to one degree of freedom at its temperature. Thus chains of electrons moving like rigid bodies may travel along the lines of the lattices, and carry electricity and energy from one part of the metal to another. The theory that electric and thermal conductivity is due to the movement of these chains is worked out, and is shown to account for the variation of electrical resistance with temperature, for the super-conductivity of metals at very low temperatures discovered by Kammerlingh-Onnes, and for Wiedemann and Franz's law of the proportion between electrical and thermal conductivity.

LIX. *The Decrease of Energy of α Particles on passing through Matter.* By G. H. HENDERSON, Ph.D.*

§ 1. *Introduction.*

THE general laws governing the passage of α particles through matter have been discussed theoretically by both Darwin† and Bohr‡.

If E , M , and V be the charge, mass, and velocity of the α particle and e and m be the charge and mass of an electron, then, when the α particle approaches an electron along a line at a distance p from it, the energy given to the electron is, by the ordinary laws of dynamics,

$$Q = \frac{2E^2e^2}{mV^2(p^2 + a^2)}, \quad \dots \dots (1)$$

where
$$a = \frac{Ee(M+m)}{MmV^2} = \frac{Ee}{mV^2} \text{ approx.,}$$

if the electron is free.

In passing through a thickness Δx of matter, the number of encounters in which p lies between p and $p + dp$ is

$$2\pi Nn\Delta x p dp,$$

where N = the number of atoms in 1 cm.³

and n = the number of electrons in one atom.

Then, if T is the energy of the α particle,

$$\frac{\Delta T}{\Delta x} = \frac{4\pi E^2e^2Nn}{mV^2} \int \frac{p dp}{p^2 + a^2} \dots \dots (2)$$

If the limits of p in this integral be taken as 0 and ∞ , the integral becomes infinite, *i. e.* an α particle could not pass through an appreciable thickness of matter at all. Evidently some upper limit to the radius of action of the α particle must be taken.

In the first paper dealing with the motion of α particles, Darwin made the assumption that the effect of the α particle at any instant was confined to the electrons of the atom through which it was passing. He was able to calculate the motion of the α particles through matter for various arrangements of electrons within the atom. Theoretical velocity curves showing the variation of velocity with distance

* Communicated by Sir E. Rutherford, F.R.S.

† Darwin, Phil. Mag. xxiii. p. 901 (1912).

‡ Bohr, Phil. Mag. xxv. p. 10 (1913), and xxx. p. 581 (1915).

travelled were obtained which showed the same general form as the experimental curves, and from these an estimate of the number of electrons in the atom was made.

On the other hand, Bohr considered the time of passage of the α particles past an electron to be the determining factor, and assumed that as long as this time of passage was small, compared with the period characteristic of the electron in dispersion phenomena, the electron could be considered as free. When the time of passage was comparable with this, however, the electron could no longer be considered as free, and in this way an upper limit to p was introduced. The calculated velocity curves showed good agreement with experiment over most of the range of the α particle.

§ 2. *Method adopted.*

In this paper the law of decrease of energy of an α particle is developed along lines somewhat different from those of the writers mentioned.

According to the modern ideas of atomic structure, due to Bohr, the electrons are thought to be arranged in various stationary states or energy levels. An electron leaving one of these stationary states can only move to another such state or completely out of the atom (to infinity). Thus the energy which an electron can take up is limited to a number of finite amounts characteristic of the atom.

These views furnish a simple method of fixing the upper limit to the radius of action of an α particle upon the electrons of matter. If the electron is to be moved from one stationary state to another by the passage of an α particle near it, then with the finite amount of energy which the electron must take up in order to effect the change there may be associated an upper limit to the radius of an α particle upon the electron.

The mechanism which is involved in this transfer of energy from α particle to electron may be difficult to conceive. However, when an electron is moved from its stationary state to infinity by the action of light, the frequency ν of the light must be such that the quantum $h\nu$ is greater than the finite difference of energy between the initial and the final states of the electron. Here the rule governing the transfer of energy is known, although the mechanism involved is not. A similar statement holds for the case when the transfer of electrons from one state to another is caused by electron impacts (elastic and inelastic impacts). Similarly, in the case of α particle impacts the transfer of

energy might be determined by appeal to experiment before the mechanism is understood.

Accordingly, it seemed of interest to apply the classical theory of the exchange of energy as given by (1) to the case of the α particle and electron, having regard to the limited number of stationary states which the electron can occupy within the atom, and to compare the resulting law of motion of the α particle with experiment.

This has been done in the following paper, taking as a basis the following assumptions.

Interchange of energy with an electron takes place according to (1) provided that the energy transferable, according to (1), is greater than the ionization potential of that electron.

Thus for any given V a definite upper limit is placed upon p by (1), where Q is equal to the ionization potential. For values of p less than this limiting value p_0 , the excess of energy over that required to remove the electron from the atom may be in the form of kinetic energy of the electron.

The existence of resonance potentials is taken into account by assuming that when the energy available according to (1) lies between the ionization and resonance potentials, or between two resonance potentials, the energy transferred is constant and equal to the lower resonance potential.

For encounters where p is greater than p_0 , given by (1) for the lowest resonance potential, it is assumed that practically no energy is transferred to the electron, the latter continuing to move in its stable orbit and behaving as if rigidly bound to the atom.

§ 3. Calculation of the Law of Motion of α Particles.

Consider a substance in each of the atoms of which there are $n_1, n_2 \dots n_r$ electrons with the ionization potentials $Q_1, Q_2 \dots Q_r$ respectively. The total number of electrons

$$n = n_1 + n_2 + \dots n_r.$$

Then, for the n_1 electrons having the ionization potential Q_1 ,

$$\frac{\Delta T}{\Delta x} = \frac{2An_1}{V^2} \int_0^{r_1} \frac{p dp}{p^2 + a^2},$$

where p_1 is given by

$$p_1^2 + a^2 = \frac{2E^2 e^2}{mV^2 Q_1}$$

and

$$A = \frac{2\pi E^2 e^2 N}{m}.$$

$$\begin{aligned} \text{Hence} \quad \frac{\Delta T}{\Delta x} &= \frac{A n_1}{V^2} \log \frac{p_1^2 + a^2}{a^2} \\ &= \frac{A n_1}{V^2} \log \frac{2mV^2}{Q_1}. \end{aligned}$$

Summing for all types of electrons,

$$\begin{aligned} \frac{\Delta T}{\Delta x} &= \frac{A}{V^2} \sum_s n_s \log \frac{2mV^2}{Q_s} \\ &= \frac{A}{V^2} [n \log 2mV^2 - \sum_s n_s \log Q_s] \end{aligned}$$

is the rate of loss of energy due to ionization potentials.

To take into account the effect of resonance potentials, consider, first, the n_1 electrons with the ionization potential Q_1 . Let there be resonance potentials $Q_1', Q_1'' \dots$, all less than Q_1 , and let the corresponding upper limits, given by (1), for the p 's be $p_1', p_1'' \dots$. We assume that for values of p lying between p_1 and p_1' (*i.e.*, when the energy available, according to (1), lies between the ionization and resonance potentials) the energy transferred to the electron is constant and equal to Q_1' . Similarly, for all values of p between p_1' and p_1'' , the energy transferred is constant and equal to Q_1'' .

Then the total loss of energy by the α particle passing through a distance Δx , which is due to the presence of resonance potentials, will be

$$\begin{aligned} \Delta T &= 2\pi N n_1 \Delta x \left[Q_1' \int_{p_1}^{p_1'} p dp + Q_1'' \int_{p_1'}^{p_1''} p dp + \dots \right], \\ \frac{\Delta T}{\Delta x} &= \pi N n_1 [Q_1' (p_1'^2 - p_1^2) + Q_1'' (p_1''^2 - p_1'^2) + \dots], \\ \frac{\Delta T}{\Delta x} &= \frac{2\pi N E^2 e^2 n_1}{m V^2} \left[Q_1' \left(\frac{1}{Q_1'} - \frac{1}{Q_1} \right) + Q_1'' \left(\frac{1}{Q_1''} - \frac{1}{Q_1'} \right) + \dots \right], \\ &= \frac{A n_1}{V^2} \sum_t \left\{ 1 - \frac{Q_1^{(t+1)}}{Q_1^{(t)}} \right\}. \end{aligned}$$

Summing this expression for all the types of electrons n_1, n_2 , etc., we have

$$\frac{\Delta T}{\Delta x} = \frac{An}{V^2} \sum_s \frac{n_s}{n} \sum_t \left\{ 1 - \frac{Q_s^{(t+1)}}{Q_s^{(t)}} \right\}.$$

Thus the complete expression for the loss of energy is

$$\frac{\Delta T}{\Delta x} = \frac{An}{V^2} \left[\log V^2 + \log 2m - \sum_s \frac{n_s}{n} \log Q_s + \sum_s \frac{n_s}{n} \sum_t \left\{ 1 - \frac{Q_s^{(t+1)}}{Q_s^{(t)}} \right\} \right].$$

$$\text{Put } \log b = \log 2m - \sum_s \frac{n_s}{n} \log Q_s + \sum_s \frac{n_s}{n} \sum_t \left\{ 1 - \frac{Q_s^{(t+1)}}{Q_s^{(t)}} \right\}. \quad (3)$$

$$\text{Then} \quad \frac{\Delta T}{\Delta x} = \frac{An}{V^2} \log b V^2.$$

Replacing T by $\frac{1}{2}MV^2$ we have in the limit

$$-MV \frac{dV}{dx} = \frac{An}{V^2} \log b V^2,$$

the negative sign entering because ΔT is a loss of energy.

$$\begin{aligned} \text{Thus} \quad dx &= - \frac{MV^3 dV}{An \log b V^2} \\ &= - \frac{MbV^2 d(bV^2)}{2Anb^2 \log b V^2} \\ &= - \frac{M}{2Anb^2} \frac{e^{-y} dy}{y}, \text{ where } y = -2 \log b V^2. \end{aligned}$$

Let the velocity of the α particle initially be V_0 and the velocity of the α particle after doing a distance x be V , then

$$x = - \frac{M}{2Anb^2} \int_{Y_0}^Y \frac{e^{-y} dy}{y},$$

$$\begin{aligned} \text{where} \quad Y &= -2 \log b V^2 = - \log b^2 V^4, \\ Y_0 &= - \log b^2 V_0^4. \end{aligned}$$

$$\text{Hence} \quad x = \frac{M}{2Anb^2} [Ei(-Y_0) - Ei(-Y)]. \quad (4)$$

$Ei(x)$ is the exponential integral, defined by

$$Ei(x) = \int_{-\infty}^{-x} \frac{e^{-u} du}{u},$$

numerical values of which have been tabulated by various writers.

It is very interesting to observe that this equation is of the same type as that derived by Bohr in his second paper on the motion of α particles through matter, although derived on quite different assumptions. The meaning of some of the constants is, of course, quite different.

§ 4. *Comparison with Experiment.*

Substituting accepted values of the physical constants we have from (4)

$$x = \frac{5.84 \times 10^{-36}}{b^2} [\text{Ei}(-Y_0) - \text{Ei}(-Y)]$$

for air at 15°C . and 760 mm. pressure, assuming the number of electrons in the fictitious air molecule to be 14.4.

We substitute numerical values in expression (4) for $\log b$, term by term,

$$\log 2m = 2.30 \log_{10} 2 \times 9.0 \times 10^{-28} = -61.58.$$

The remaining two terms are more difficult to evaluate, as the values of the ionization and resonance potentials are not completely known, and we are treating with average values for air. The order of magnitude of these quantities is, however, fairly well established. We will choose values of this order of magnitude which give the best agreement with experiment.

Assuming 4 electrons for which $Q=200$ volts $= 3.18 \times 10^{-10}$ erg and 10.4 electrons for which $Q=15$ volts $= 2.38 \times 10^{-10}$ erg,

$$-\sum_s n_s \log Q_s = -2.3 \left[\frac{10.4}{14.4} \log_{10} 2.38 \times 10^{-11} + \frac{4}{14.4} \log 3.18 \times 10^{-10} \right] = 23.75.$$

For values of the resonance potential which are near the ionization potential the terms $(1 - Q_s^{(t+1)}/Q_s^{(t)})$ will be practically zero. Hence we need only concern ourselves with those few resonance potentials which are considerably lower than the ionization potential. We shall probably not be far wrong if we set $\sum_t (1 - Q_s^{(t+1)}/Q_s^{(t)}) = 2$ for each set of electrons.

Then $\log b = -61.58 + 23.75 + 2.0 = -35.83$,

$$\log b^2 = -71.66,$$

corresponding to a value of $b^2 = 7.5 \times 10^{-32}$ approximately.

Thus the velocity equation of the α particle becomes

$$x = 7.79 \times 10^{-5} [\text{Ei}(-Y_0) - \text{Ei}(-Y)].$$

It should be pointed out that since b appears as well in the exponential integrals, the value of x is not very sensitive to changes in b .

Values of the range given by the formula have been calculated for various velocities of the α particle, and the results are shown in the second column of Table I. The evaluation of $Ei(-Y)$ has been carried out by interpolation from the tables given by Jahnke and Emde*. In column three are given the experimental results of Marsden and Taylor†. Column four shows the ranges as calculated by Bohr‡. The Table refers to RaC in air at 15° C.

TABLE I.

V/V_0 .	Calc.	Experimental.	Calc. Bohr.
·9	1·87	1·90	1·89
·8	3·43	3·34	3·35
·7	4·50	4·48	4·48
·6	5·23	5·32	5·35
·5	5·67	5·97	5·97

From the table it will be seen that the calculated values agree well with experiment. Both series of calculations fail for low velocities of the α particles. Bohr's theory holds down to values of V/V_0 equal to about ·5; the present theory has not quite the same range of applicability, failing below values of V/V_0 of about ·6.

One or two points of interest should be noticed here. First, we shall see what is the actual size of the radius of action of the α particle called for. Taking an α particle moving with the initial velocity of radium C ($1\cdot92 \times 10^9$ cm./sec.) and a resonance potential of 10 volts, when numerical values are substituted in (1), we obtain

$$p_0^2 + a^2 = 7\cdot85 \times 10^{-18}, \quad a^2 = 1\cdot89 \times 10^{-20},$$

and hence

$$p_0^2 = 7\cdot83 \times 10^{-18},$$

Thus, $p_0 = 2\cdot80 \times 10^{-9}$ cm. is the distance from the electron within which an α particle must come in order to transfer to it energy corresponding to 10 volts. This distance is of the order of one-tenth of the diameter of an atom.

Secondly, there will be a velocity below which the α particle will be unable to ionize, however close the collision. As the velocity of the α particle decreases the value of p_0 increases

* Jahnke u. Emde, *Funktionentafeln*, p. 19.

† Marsden and Taylor, *Proc. Roy. Soc. A.* 88, p. 443 (1913).

‡ Bohr, *Phil. Mag.* xxx. p. 597 (1915).

at first in inverse proportion to the velocity. A time will come, however, when the term in a^2 will become important, the value of p_0 will then begin to fall off rapidly to zero at a finite value of V , which may be called the critical velocity V_c . For the ratio $(p_0^2 + a^2) / a^2 = 2mV^2 / Q$ must not be less than unity. When it is equal to 1, $p_0 = 0$.

Then $V_c^2 = Q/2m = 8.8 \times 10^{15}$.

The critical velocity $V_c = 9.4 \times 10^7$ cm/sec.

The same results should hold for positively charged hydrogen atoms, which should cease to ionize a gas of 10 volts ionization potential at velocities less than about 10^8 cm./sec., equivalent to about 5000 volts. This point has been discussed by Sir J. J. Thomson*, who has dealt with the problem of the ionization produced by moving electrified particles along somewhat the same lines as that followed in this paper, by assuming that a definite amount of energy is necessary to remove an electron from an atom. It appears from experiment that positive rays cease to ionize only when their energy is less than 1000 volts. This is not surprising, since at these low velocities the velocity of the electron itself probably plays an important part.

§ 5. Conclusion.

From the figures given in Table I. it will be seen that the theory developed in this paper gives good agreement with experiment in air for α particle velocities which are not too low. It has already been pointed out that both Bohr's and the present theories lead to equations of the same type (4). In both cases constants of the proper order of magnitude give good agreement. These constants are adjustable, but it should be pointed out that their orders of magnitude are fairly well known, and hence they are adjustable only within narrow limits. It seems a little surprising that practically the same results should be arrived at, starting from such different assumptions. It is possible that these views might be assimilated when more is known about the actual mechanism of the transfer of energy from α particle to electron.

Unfortunately the exponential integral which occurs in the final equation of motion is of such a character that a certain amount of variation in the values of the constants employed does not materially affect the agreement with experiment. It is thus impossible to decide definitely by appeal to experiment which of the two points of view adopted is the more correct.

* Thomson, 2nd Solvay Congress, 1913.

For the same reason calculations have not at present been carried out for substances other than air. In this connexion the remarkable agreement obtained by Bohr in the case of hydrogen, making use only of known data, should not be lost sight of. Unfortunately, data regarding resonance and ionization potentials for gases in the molecular state are still incomplete.

It is regretted that results of a more decisive character have not as yet developed from this application of the concepts of resonance and ionization potentials. However, it is felt that the possibility of explaining, along the lines followed here, much of the experimental data on the motion of α particles should be pointed out. The equation of motion is obtained comparatively simply, as will be seen from § 3.

The above remarks concerning agreement with experiment referred to velocities not lower than $\cdot 5V_0$, half the initial velocity of RaC. For velocities lower than this the agreement breaks down completely. This is only to be expected, for experimental data of other kinds show that the previous homogeneity of the beam of α particles begins to disappear at about this velocity.

In the foregoing calculation no account has been taken of probability variations in the beam, while from a velocity of $\cdot 5V_0$ downwards these variations become marked. Neither has account been taken of the orbital velocities of the electrons which may become appreciable for low α particle velocities. Experiment shows that the beam becomes anhomogeneous in velocity. Straggling becomes very large at this point. Further, recent results obtained by the writer give evidence to show that the charge on the α particle does not remain invariable for low velocities, though further discussion of this point must be reserved. All things considered it seems clear that the behaviour of a beam of α particles becomes much too complicated at low velocities to be dealt with by simple treatment.

Summary.

In this paper the equation of motion of an α particle passing through matter is developed, making use of the concepts of resonance and ionization potentials.

The equation found is shown to give good agreement with experiment in the case of air, but does not furnish a decisive test when compared with other solutions which have been proposed.

Cavendish Laboratory,
July 1922.

LX. *A Kinetic Theory of Adsorption.*

By D. C. HENRY *.

UP to the present time no theory of adsorption has been developed which leads to equations valid over the whole range from low to high concentrations. The adsorption, both of gases and of solutes from solution, is well expressed for low concentrations by the empirical "exponential formula"

$$\alpha = k \cdot c^{\frac{1}{n}},$$

where α denotes the quantity adsorbed, c the exterior concentration, and k and $\frac{1}{n}$ are constants. As soon as moderately high concentrations of adsorbate are reached, this formula gives results greatly in excess of the values observed, which appear to tend to an upper limit.

In the present paper a theory of adsorption is developed based on the conceptions of surface action introduced by Hardy and Langmuir. An adsorption equilibrium is considered as involving a balance between the rate at which molecules of adsorbate condense on the surface of the adsorbent and the rate at which molecules leave, or evaporate from the same surface. The fundamental assumptions made are two, for both of which Langmuir has produced much evidence. In the first place, it is assumed that the range of action of the forces which bind molecules of adsorbate on to the adsorbing surface is comparable with the diameter of an atom, so that the layer of adsorbate molecules bound by the field of force of the adsorbent will be only one molecule thick. Secondly, it is assumed that the impact of a molecule on a surface is completely inelastic, so that every impinging molecule will condense.

General Adsorption Equation for n Gaseous components.

Consider an adsorbing surface, of area ω , brought into contact with a homogeneous gaseous phase containing n components $S_1, S_2, \dots S_n$. Whether the surface be crystalline or liquid, it will present a more or less regular arrangement of points of unsaturated field of force, where molecules of adsorbate can condense; if the surface is crystalline, the arrangement will be related to the crystal lattice, if it is liquid, to the packing of the oriented surface molecules.

* Communicated by Prof. S. Chapman, F.R.S.

Suppose there are N_0 such points of attachment. If a molecule from the gaseous phase impinges on a point of attachment unoccupied by any other adsorbed molecule, it will condense, forming a single "adsorbed layer"; if it impinges on a point already occupied, it will also condense, forming a second layer. But the relative life of a molecule on the surface will depend on the attractive force exerted on it by the surface, and if, as is usually the case, the attractive force between molecules of adsorbent and adsorbate is much greater than that between two molecules of adsorbate, the relative life of a molecule in the second layer will be so small compared with that of a molecule in the first layer, that we may treat molecules impinging on points already occupied as if they were immediately reflected and never condensed.

At any moment let a fraction θ_0 of the points of attachment be vacant, and fractions $\theta_1, \theta_2, \dots \theta_n$ be covered with monomolecular layers of $S_1, S_2, \dots S_n$ respectively; then

$$\theta_0 + \theta_1 + \theta_2 + \dots + \theta_n = 1. \quad (1)$$

Let a single molecule of $S_1, S_2, \dots S_n$ occupy respectively $a_1, a_2, \dots a_n$ points of attachment*; the number of molecules of component S_r adsorbed will be $\frac{\theta_r N_0}{a_r}$, and the adsorbed quantity in gram-molecules will be

$$X_r = \frac{\theta_r N_0}{a_r N}, \quad (2)$$

where N is Avogadro's constant (6.06×10^{23}).

Now the rate of evaporation from the surface will be determined by Maxwell's distribution law as the number of molecules which reach, per second, a state of agitation sufficient to break free from the force field, and is given, for S_r , in gram-molecules per second, by the expression †

$$A_r \sqrt{T} \cdot e^{-\frac{\lambda_r}{RT}} \cdot X_r = (\text{say}) \nu_r X_r, \quad (3)$$

where λ_r is the internal heat of evaporation of S_r from the surface, A_r is a constant depending on the field of force, and R and T have their usual meanings; ν_r is written for the expression

$$A_r \sqrt{T} \cdot e^{-\frac{\lambda_r}{RT}}.$$

* Since the number of points of attachment occupied by a molecule is not subject to a merely geometrical restriction, but is determined by the field of force, it does not appear essential that the quantities a_r should be integers.

† Langmuir, Jour. Amer. Chem. Soc. xxxv. p. 122 (1913). Richardson, Phil. Trans. A. cci. p. 501 (1903).

Now if p_r is the partial pressure of S_r in the gaseous phase, the rate of impact of molecules of this component is *

$$\sqrt{\frac{1}{2\pi RTm_r}} \times p_r \text{ gm.-molecules per second per sq. cm.,}$$

where m_r is the molecular weight of S_r ; hence the rate of impact on the surface of area ω is ω times this quantity, which may be written

$$\omega \mu_r p_r \text{ gm.-molecules per second.} \quad (4)$$

For a molecule of S_r to condense, it must impinge on a spot where there are a_r vacant adjacent points of attachment. The chance that a given molecule will find one point vacant is θ_0 , and the chance that it will find a_r adjacent vacant points will be $\theta_0^{a_r}$, if we neglect the possibility that the molecule may need to impinge in an orientation related to the configuration of the vacant points†. Hence the rate of condensation of molecules of S_r is

$$\omega \mu_r p_r \theta_0^{a_r} \text{ gm.-molecules per second.} \quad (5)$$

For equilibrium, the expression (4) must equal the expression (5), and we get the n equations

$$\nu_r X_r = \omega \mu_r p_r \theta_0^{a_r} \quad r=1, 2, \dots n;$$

or, from (1)

$$X_r = \omega \frac{\mu_r}{\nu_r} p_r (1 - \theta_1 - \theta_2 - \dots \theta_n)^{a_r},$$

which from (2)

$$\begin{aligned} &= \omega \frac{\mu_r}{\nu_r} p_r \left[1 - \frac{a_1 N}{N_0} X_1 - \dots - \frac{a_n N}{N_0} X_n \right]^{a_r} \\ &= \zeta_r p_r \left[1 - \frac{X_1}{X_1'} - \dots - \frac{X_n}{X_n'} \right]^{a_r}, \quad (6) \end{aligned}$$

where ζ is written for

$$\omega \frac{\mu_r}{\nu_r} = \frac{\omega}{A_r} \sqrt{\frac{1}{2\pi Rm_r}} \cdot \frac{1}{T} \cdot e^{\frac{\lambda_r}{RT}}, \quad (7)$$

and

$$X_r' = \frac{N_0}{a_r N}, \quad (8)$$

and is therefore the saturation capacity of the surface for S_r , supposing it to be completely covered by a monomolecular layer of that component.

* Jeans, 'Dynamical Theory of Gases,' 1916, p. 133. Langmuir, Phys. Rev. ii. p. 331 (1913).

† This possibility could probably be allowed for by multiplying $\theta_0^{a_r}$ by a constant depending on a_r , which could then be included in ζ_r .

The n relations (6) determine the equilibrium adsorptions of the n components.

In a similar manner we can write for the velocity of adsorption of S_r in gm.-molecules per second

$$\frac{dx_r}{dt} = \omega \mu_r p_r \left[1 + \frac{x_1}{X_1} + \dots + \frac{x_n}{X_n} \right]^{a_r} - v_r x_r, \quad (9)$$

where x_r is the instantaneous value of the adsorption of S_r at time t , and p_r is the instantaneous value of the corresponding partial pressure. A similar relation holds for each of the n components.

The Temperature Coefficient of the Isotherm.

The effect of temperature on the equilibrium adsorption follows from equation (6), the only constant of which that involves the temperature being ζ , which from equation (7) is given by

$$\zeta = \zeta_0 \cdot \frac{1}{T} \cdot e^{\frac{\Lambda}{kT}}, \quad (10)$$

where ζ_0 is a constant independent of the temperature. The qualitative conclusion that adsorption decreases with rise of temperature follows immediately.

The relations (6) and (9) do not admit of general solutions. Solutions must therefore be obtained for special cases.

One Component only—Adsorption of a single Gas.

Equation (6) reduces to

$$X = \zeta p \left[1 - \frac{X}{X'} \right]^a, \quad (11)$$

which can be expressed

$$\begin{aligned} \ln \frac{X}{p} &= \ln \zeta + a \cdot \ln \left[1 - \frac{X}{X'} \right] \quad (12) \\ &= \ln \zeta - a \left[\frac{X}{X'} + \frac{1}{2} \cdot \frac{X^2}{X'^2} + \dots \right]. \end{aligned}$$

For moderately small adsorptions we can use the approximation

$$\ln \frac{X}{p} = \ln \zeta - \frac{a}{X'} X,$$

or
$$\log \frac{X}{p} = \log \zeta - 0.4343 \cdot \frac{a}{X'} \cdot X. \quad (13)$$

The relation (13) is of the same form as that obtained by

Williams* from entirely different assumptions, and can be tested with the help of Williams's calculations of the measurements of Titoff, Homfray, and Chappuis. Reducing the equation to his units (adsorption α in c.c. of gas at N.T.P., pressures in cm. of mercury), we obtain

$$\log \alpha = \log (2.988 \cdot 10^8 \cdot \zeta) - 0.4343 \cdot \frac{a}{\alpha} \cdot \alpha$$

$$= A_0 - A_1 \alpha \dots \dots \dots (14)$$

The agreement found is very good, as is shown in the following table:—

TABLE I.

	Number of Observations.	Mean divergence of observed results from those calculated by equation (14).	by "exponential formula."
Nitrogen (Titoff).....	8	0.9 per cent.	7.0 per cent.
Methane (Homfray)	8	0.6 "	4.4 "
Carbon monoxide (Homfray) ...	10	0.8 "	7.0 "
Carbon dioxide (Chappuis) up to an absorption of 40 per cent. saturation, (excluding one reading)	49	0.8 "	—

Above 40 per cent. saturation, as might be expected, the approximation (14) ceases to hold exactly.

I have also applied relation (14) to some measurements of Schmidt† on the adsorption of vapours of charcoal; these observations are not very precise (they do not lie evenly on any smooth curve), but for fairly low concentrations reasonable agreement is found. In fig. 1, $\log \alpha/p$ is plotted against α for three series.

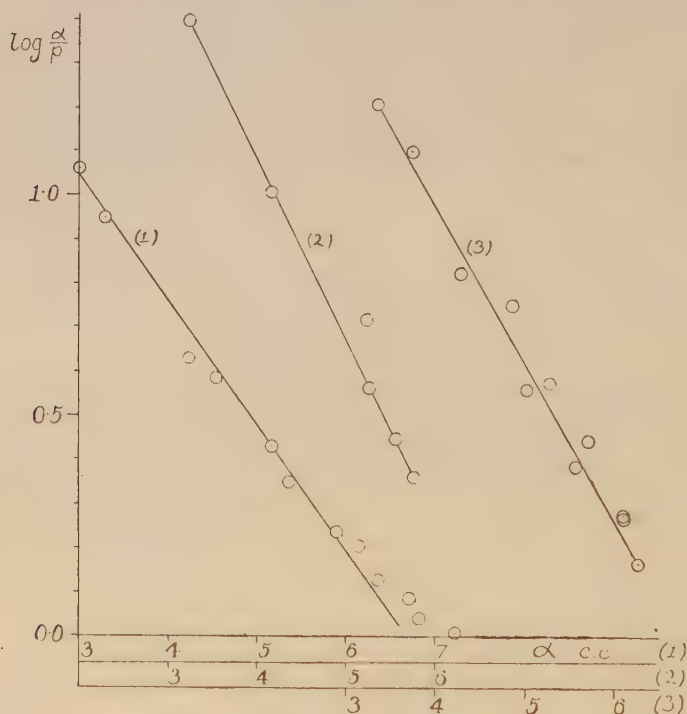
From the experimentally determined values of the constants A_0 and A_1 , values can be obtained for ζ , a , and N_0 . These are shown in Table II. The values for a are positive small quantities, and, moreover, for the four gases the relative magnitudes are as would be expected, small for the inactive nitrogen, which cannot saturate much of the field of force, intermediate for methane and carbon dioxide, and largest for the unsaturated carbon monoxide. The values for ζ , which is a measure of the relative stability of the molecules on the surface, also follow the same sequence, the inactive gases having the shortest life on the surface. Finally, the

* A. M. Williams, Proc. Roy. Soc. A. xevi. p. 287 (1919).

† Schmidt, Zeit. f. Phys. Chem. xci. p. 115 (1916).

values obtained for N_0 per gram of charcoal are of the same, and that a reasonable, order of magnitude.

Fig. 1.



Schmidt's Observations on the Adsorption of Vapours.

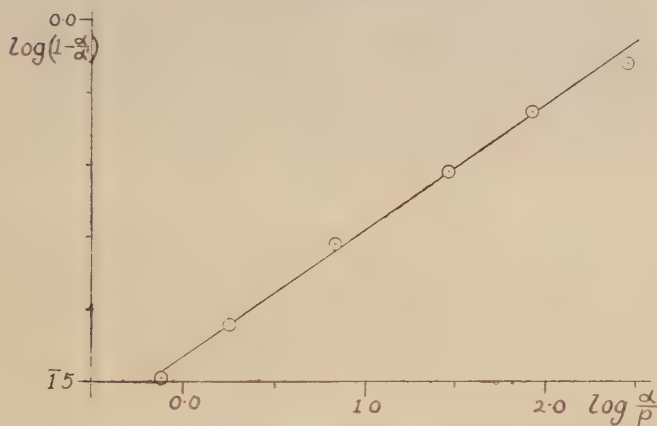
(1) Carbon disulphide. (2) Benzene. (3) Chloroform.

TABLE II.

Gas.	T° C.	Observer.	a .	$\frac{a}{p}$ per gm. charcoal.	N_0 per gm. charcoal.
Nitrogen	0	Titoff	3.16	8.72×10^{-10}	8.22×10^{20}
Methane	0	Homfray	3.72	4.89×10^{-9}	7.12×10^{20}
Carbon Dioxide.....	0	Chappuis	3.32	1.47×10^{-9}	6.04×10^{20}
Carbon Monoxide...	-82	Homfray	4.74	3.17×10^{-6}	5.37×10^{20}
Benzene	15	Schmidt	5.22	6.03×10^{-6}	8.90×10^{20}
Hexane	15	"	5.53	2.95×10^{-6}	5.99×10^{20}
Carbon Disulphide.	15	"	5.28	1.86×10^{-6}	10.36×10^{20}
Chloroform	15	"	5.79	6.30×10^{-6}	11.59×10^{20}
Acetone	15	"	4.75	2.34×10^{-6}	5.52×10^{20}

In order to obtain more direct evidence of the validity of the un-approximated formula (11), I have applied it to observations of Travers * on the adsorption of carbon dioxide by charcoal, in which an adsorption 68 per cent. of saturation is reached, and to some measurements by Langmuir † on the adsorption of methane and carbon monoxide at low temperatures, in which adsorptions were reached respectively 85 per cent., 77 per cent., and 59 per cent. of the saturation values. Fig. 2, in which $\log \alpha/p$ is plotted against $\log (1-\alpha/\alpha')$, represents Travers's measurements at $-78^{\circ}2$ C.

Fig. 2.



Travers's Observations on the Adsorption of Carbon Dioxide
by Charcoal at $-78^{\circ}2$ C.

In equation (11), if a is put equal to unity, we obtain an equation of the same form as one used by Langmuir in the paper quoted for most of his experiments, and with which he finds good agreement. For three experiments, however (Tables 9, 13, and 16 of the paper quoted), he has to use a more complicated formula based on the assumption of two distinct kinds of points of attachment. Equation (11), which makes no such assumption, is found to fit these results about as well as Langmuir's equation, as is shown in

* Travers, Proc. Roy. Soc. A. lxxviii. p. 9 (1906).

† Langmuir, Jour. Amer. Chem. Soc. xl. p. 1382 (1918).

the following Tables, where α is calculated both by the latter equation, and by equation (11).

TABLE III.

p bars.	α (obs.) c.mm.	Calculated by Langmuir.		Calculated by equation (11).	
		α .	Divergence.	α .	Divergence.
<i>Methane by Mica at 90° A.</i>					
122.0	104.0	101.6	-2.4	103.5	-0.5
83.0	98.6	98.5	-0.1	98.9	+0.3
45.0	90.2	91.6	+1.3	90.1	-0.1
25.8	82.2	82.2	0.0	80.1	-2.1
17.3	71.2	73.5	+2.3	72.0	+0.8
12.8	60.6	65.9	+5.3	65.0	+4.4
8.0	52.7	53.6	+0.9	54.2	+1.5
5.2	43.7	41.8	-1.9	44.0	+0.3
3.7	36.3	33.8	-2.6	36.3	0.0
2.7	30.6	27.0	-3.6	30.9	+0.3
<i>Carbon Monoxide by Glass at 90° A.</i>					
61.6	20.0	20.2	+0.2	20.4	+0.4
31.5	18.5	18.4	-0.1	18.3	-0.2
17.3	16.2	16.2	0.0	16.2	0.0
9.3	14.0	13.9	-0.1	13.7	-0.3
5.8	11.8	11.9	+0.1	11.6	-0.2
2.7	9.6	9.6	0.0	7.9	-1.7
1.4	8.3	8.2	-0.1	4.7	-3.6
<i>Methane by Glass at 90° A.</i>					
67.0	20.3	20.2	-0.1	20.3	0.0
34.8	17.3	17.5	+0.2	17.1	-0.2
19.3	14.3	14.4	+0.1	14.2	-0.1
11.6	11.3	11.5	+0.2	12.0	+0.7
7.0	9.0	8.9	-0.1	8.9	-0.1
3.4	6.14	5.98	-0.16	6.14	0.00
1.9	4.35	4.42	+0.07	4.20	-0.16

The Influence of Temperature on the Adsorption Equilibrium.

From (10) and (11) we obtain, if X is maintained constant,

$$p = \xi \cdot T \cdot e^{-\frac{\lambda}{RT}},$$

where ξ is independent of the temperature. Transforming

the unit of pressure to cm. of mercury, and taking logarithms.

$$\begin{aligned}\log \frac{P}{T} &= \log (7.52 \times 10^{-8} \times \xi) - 0.4343 \frac{\lambda}{RT} \\ &= B_0 - \frac{B_1}{T}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)\end{aligned}$$

λ , and therefore B_1 , is a function of the temperature, but may probably be taken as constant over a fairly limited range of temperature. Over a wider range, it can probably be expressed

$$\lambda = \lambda_0 - \beta T,$$

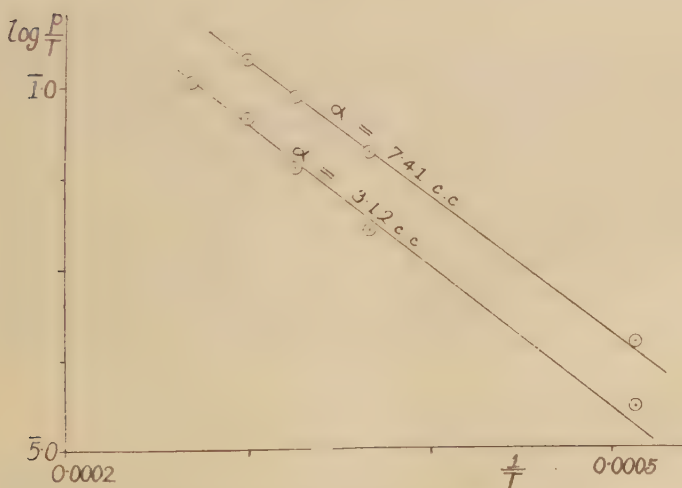
which leaves (15) of the same form, B_1 being then equal to

$$0.4343 \frac{\lambda_0}{RT}.$$

An isostere of the form (15) is not peculiar to

the present theory; Williams (*loc. cit.*) has found the same relation from his assumptions, and a similar form can be derived from Perrin's radiation hypothesis.

Fig. 3.

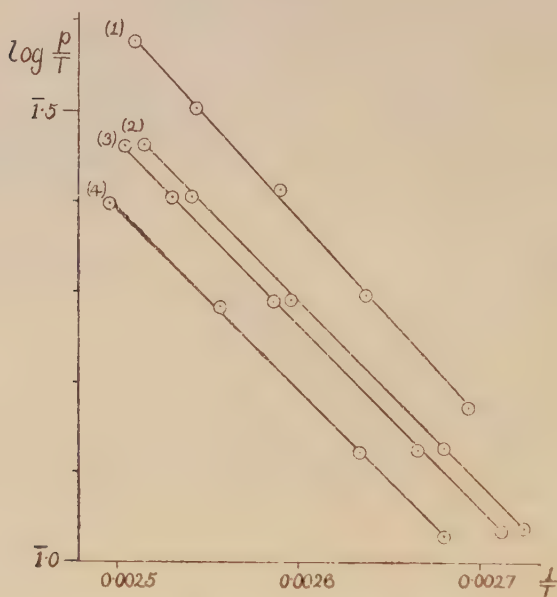


The Isostere, from Travers's Observations.

Williams has shown excellent agreement with (15) for a large number of observations of Chappuis, Homfray, and Richardson; argon and ammonia deviate at low temperatures. I have found fair agreement with the measurements of Travers (fig. 3), and excellent agreement with the

observations of Brown* on the adsorption of water vapour (fig. 4).

Fig. 4.



The Isostere, from Brown's Observations.

- (1) $\alpha = 3.35$ gms. (2) $\alpha = 2.70$ gms. (3) $\alpha = 2.00$ gms.
(4) $\alpha = 0.57$ gm.

From the empirically found values of B_1 , λ can be deduced. Table IV. shows the values so found for various adsorbing systems, and for comparison, where it is known, the value of $Q - RT$, where Q is the total heat of adsorption experimentally determined.

Two Components—Adsorption of Mixed Gases.

For moderately small concentrations, relations can be deduced from equation (6) which express the mutual influence of two gases on each other's adsorption. Since no experimental results are available to test these adequately, they are merely quoted for reference:—

I. X_1 , X_2 represent the actual adsorptions of the two components under partial pressures p_1 and p_2 . p_{10} denotes the

* Brown, Phys. Rev. xvii. p. 700 (1921).

pressure of component 1 which would produce the same adsorption X_1 in the absence of component 2, and similarly for p_{20} . Then

$$p_1 = p_{10} e^{a_1 X_2 / X_2'}$$

and

$$p_2 = p_{20} e^{a_2 X_1 / X_1'}$$

TABLE IV.

Gas.	Absorbent.	Observer.	λ cal.	Q—RT cal.
Argon.....	Charcoal	Homfray	3690	3090 (Dewar)
Methane.....	"	"	4800	
Carbon Dioxide...	"	Chappuis	6390	}
Carbon Dioxide...	"	Travers	7140	
$\alpha=3.12$ c.c....			7340	
$\alpha=7.41$ c.c....				
Mean of the three.....			6950	6700 (Chappuis)
Ammonia	Charcoal	Richardson	7440	7800 (Chappuis)
Water Vapour ...	"	Brown		
$\alpha=3.35$ gms. ...			10130	
$\alpha=2.70$ gms. ...			9580	
$\alpha=2.00$ gms. ...			9460	
$\alpha=0.57$ gm. ...			9305	
Argon.....	Mica	Langmuir	611	
Oxygen	"	"	651	
Nitrogen	"	"	889	
			1223	
			1397	
Methane... ..	"	"	1618	
			1690	
Carbon Monoxide	"	"	2155	

II. X_{10} denotes the adsorption of component 1 in the absence of component 2, component 1 being at pressure p_1 ; similarly for X_{20} . X_1 and X_2 denote as before the adsorptions in a mixed system of partial pressures p_1 and p_2 . Then *

$$X_1 = X_{10} e^{-a_1 X_2 / X_2'}$$

and

$$X_2 = X_{20} e^{-a_2 X_1 / X_1'}$$

III. Combining the above, we have for constant X_2 ,

$$X_1 p_1 = X_{10} p_{10},$$

and for constant X_1 ,

$$X_2 p_2 = X_{20} p_{20}.$$

* These relations have been roughly verified on observations of Bakr & King (Jour. Chem. Soc. cxix, p. 453 (1921)).

Adsorption from Solution.

The derivation of the adsorption relations used above depends on the kinetic theory of gases, and cannot be applied to adsorption from solution. It appears, however, to be a thermodynamic necessity that an adsorbent which is in equilibrium with a (mixed) liquid phase, should also be in equilibrium with the saturated vapour phase above the liquid. Williams* has found experimental confirmation of this assumption, and I am at present carrying out further experiments to test it. If it is valid, the adsorption equilibrium in solution is determined by a combination of equations (6) with the vapour pressure relations of the solution. Duhem's equation and Margule's integration of it both lead to expressions too complicated to test experimentally, but the special cases of (1) a dilute binary mixture, and (2) a mixture giving a linear vapour pressure-concentration curve (Dolezalek's normal mixtures) may be amenable to experimental verification.

Adsorption from dilute solutions.

For a dilute solution, we have for the solute, by Henry's law,

$$p_1 = kc_1 \quad (c_1 \text{ denotes volume concentration}),$$

and for the solvent, by Raoult's law, if P_2 is the vapour pressure of pure solvent,

$$\frac{P_2 - p_2}{P_2} = C_1 \quad (C_1 \text{ denotes molecular concentration}) \\ = 1 - C_2,$$

so that $p_2 = P_2 C_2$.

Now in dilute solution, both c and C are practically proportional to η , the concentration in grams per gram solution. Combining with equation (6), transforming the unit of amount adsorbed to grams, and collecting the constants, we get

$$u_1 = h_1 \eta_1 \left[1 - \frac{u_1'}{u_1'} - \frac{u_2'}{u_2'} \right]^{a_1}, \\ u_2 = h_2 \eta_2 \left[1 - \frac{u_1'}{u_1'} - \frac{u_2'}{u_2'} \right]^{a_2},$$

where u_1 , u_2 represent the true adsorptions of solute and solvent respectively, u_1' and u_2' the corresponding saturation

* Williams *Medd. f. K. Vet.-Akad. Nobelinstitut*, ii. No. 27, p. 2.

adsorptions. The apparent or observed adsorption of the solute will be (Williams *)

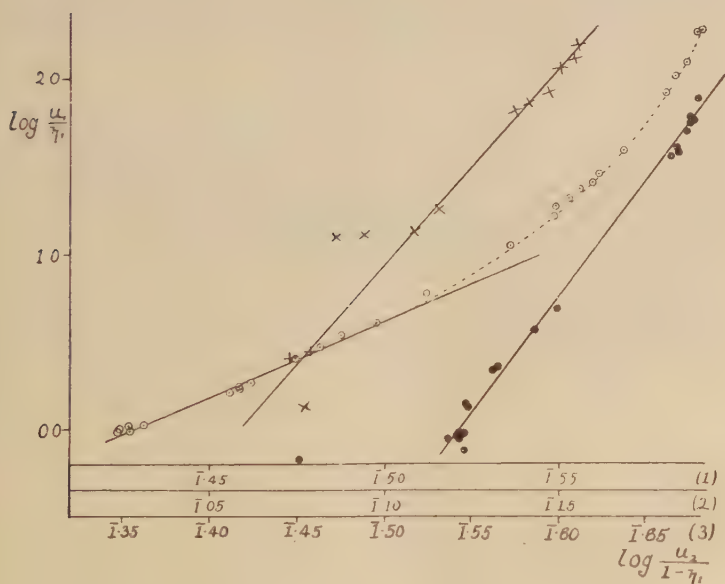
$$u_0 = u_1 - \frac{\eta_1}{\eta_2} u_2.$$

For small concentrations η_1 , u_0 is practically identical with u_1 , and the apparent adsorption may be used for the true adsorption. For higher concentrations, the true adsorptions can be calculated from the apparent adsorption by use of equation (17) together with the empirical relation of Williams (*loc. cit.*),

$$\frac{u_1}{u_{1\infty}} + \frac{u_2}{u_{2\infty}} = 1,$$

where $u_{1\infty}$ and $u_{2\infty}$ denote the adsorptions from pure solute and solvent respectively (determined by weighing after adsorption from the vapour phase).

Fig. 5.



Williams's Observations on the Adsorption of Acetic Acid.

(1) O Williams's Table 11; (2) x Table 12; (3) ● Table 13.

From equations (16) we deduce

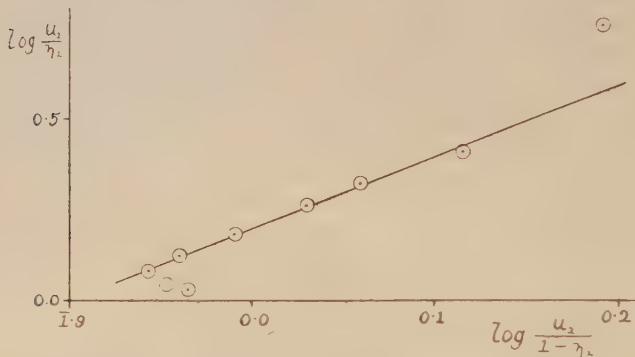
$$\log \frac{u_1}{\eta_1} - \frac{a_1}{a_2} \log \frac{u_2}{\eta_2} = \log h_1 - \frac{a_1}{a_2} \log h_2 = \text{constant},$$

so that plotting $\log u_1/\eta_1$ against $\log u_2/\eta_2$ should give a straight line. Figs. 5 and 6 represent the results of plotting

* *Loc. cit.*

in this way some results of Williams and of Gustafson*. Though the agreement is not perfect, the straight line fits the observations for low concentrations as well as any line.

Fig. 6.



Gustafson's Observations on the Adsorption of a Phenol-Alcohol Mixture.

No observations are available for testing these relations with a mixture of linear vapour pressure-concentration curve.

A Derivation of the "Exponential Formula" for the Adsorption Isotherm.

The relation

$$\alpha = kc^n$$

has hitherto had no theoretical basis, but represents experimental results very well for low concentrations. By a method based on the same assumptions as those employed in the earlier part of this paper, this formula can be put on a theoretical basis.

Consider the adsorption of a gas. Let the free surface energy of the bare surface (*i. e.* the surface in contact with a vacuum) be σ_0 ergs per sq. cm., and let the free surface energy of the same surface covered with a monomolecular layer of gas be σ_1 . In adsorption equilibrium, let a fraction θ of surface be covered, and let the free energy of the whole surface be σ ergs per sq. cm.

Then, since the range of molecular action is assumed small,

$$\sigma = \sigma_0(1 - \theta) + \sigma_1\theta = \sigma_0 - (\sigma_0 - \sigma_1)\theta.$$

* Gustafson, *Zeit. f. Phys. Chem.* xci. p. 385 (1916); *Zeit. f. Electrochem.* xxi. p. 459 (1915).

But $\theta = X/X'$, and

$$\sigma = \sigma_0 - \frac{\sigma_0 - \sigma_1}{X'} X.$$

But X is identical with Gibbs's "surface excess," Γ , and σ is numerically identical with the surface tension; by Gibbs's equation, for small concentrations,

$$X = - \frac{c}{RT} \cdot \frac{d\sigma}{dc} = \frac{c}{RT} \cdot \frac{\sigma_0 - \sigma_1}{X'} \cdot \frac{dX}{dc},$$

which on integration gives

$$\ln X = \frac{RTX'}{\sigma_0 - \sigma_1} \cdot \ln c + \ln k,$$

where $\ln k$ is an integration constant.

If we write

$$\frac{RTX'}{\sigma_0 - \sigma_1} = \frac{1}{n},$$

this becomes

$$X = kc^{\frac{1}{n}},$$

which is the "exponential formula."

The same argument applies to adsorption from a dilute solution, where σ_0 is taken as the free surface energy of the surface in contact with pure solvent, and the apparent adsorption (to which Gibbs's relation applies) is taken equal to the true adsorption, which is permissible in dilute solution.

The exponent

$$n = \frac{\text{osmotic work in adsorption of } X' \text{ gm.mol.}}{\text{total work in adsorption of } X' \text{ gm.mol.}}$$

$$= \frac{RTX'}{RTX' + WX'} = \frac{RT}{RT + W},$$

where W is the non-osmotic work in the adsorption of 1 gm. mol.; this is probably accounted for by the work done in the orientation of the surface molecules, and is not likely to vary much with temperature. It follows that $\frac{1}{n}$ is a quantity

always less than unity, which tends towards unity with rise of temperature. This is in accord with experience.

$$\text{Again,} \quad n - 1 = \frac{W}{RT},$$

so that, at a given temperature, the greater the orientational

work the larger will n be. This is in accord with experiment, for we find that the larger the molecule of adsorbate, the larger is n , as exemplified by the following Table for various substances adsorbed on charcoal.

TABLE V.

Gases.	n .	Solutes.	n .
Hydrogen	1 to 2	Formic Acid	2.22
Nitrogen		Acetic Acid	2.35
Oxygen		Propionic Acid	2.54
Carbon Dioxide...	2.47 (Chappuis)	Butyric Acid	3.32
Sulphur Dioxide.	3.09 "	Benzoic Acid.....	2.72
Chlormethyl	8.2 "	Picric Acid.....	4.17
		Benzenesulphonic Acid	4.48
		New Fuchsin	5.38
		Crystal Ponceau	6.67
		Cane Sugar	8.2 (Bancroft)
(Data, except where specified, from Freundlich, <i>Kapillarchemie</i> , p. 150.)			

We should expect that the value of W would increase in the same sequence for a series of adsorbates on different adsorbents, since the orientational work will be chiefly due to orientation of the adsorbate molecules. This is approximately the case (Freundlich, *Kapillarchemie*, p. 155).

It would be interesting to compare the values of W obtained from the exponential formula with the work done when two unit surfaces of two liquids come together (Harkins *), but as far as I am aware, there are no experimental data for the adsorption isotherm on liquid adsorbents.

Summary.

1. A theory of adsorption of gases has been developed on a kinetic basis by means of assumptions derived from Langmuir's conception of a monomolecular layer.

2. Equations for the adsorption isotherm and isostere are deduced which are in satisfactory agreement with experiment.

3. A method is suggested for applying these equations to adsorption from solution, and the results compared with experimental data.

* Harkins, Jour. Amer. Chem. Soc. xxxix. p. 541 (1917).

4. A theoretical derivation for the "exponential formula" is given, which attributes to the exponent $1/n$ a theoretical significance which is in qualitative agreement with experience.

It is not claimed that the theory advanced is a complete solution of the problem, or that it is valid in all cases, but the agreement obtained is sufficient to indicate that the mechanism of adsorption suggested may be an approximation to the truth.

The work contained in this paper was done while the author was "Coutts Trotter" student of Trinity College, Cambridge.

LXI. *On Electromagnetic Lines and Tubes.* By S. R. MILNER, D.Sc., F.R.S., Professor of Physics, The University, Sheffield*.

IN a recent paper Professor Whittaker † has shown that it is possible to extend the conception of the tubes of force of electrostatic and magnetostatic fields to the general electromagnetic field, when this is considered as a four-dimensional entity. The differential equations which express the properties of the calamoids, or surfaces from which the tubes are formed, are rather complex, and it is not easy to see from them in their general form a clear picture of what the tubes really are. It is hoped that the treatment of the question contained in the following paper may be of use, as it not only enables such a picture of the position and direction in hyperspace of the tubes to be formed, but it also extends Whittaker's results in certain respects.

§ 1. *The Construction of Electromagnetic Lines.*

In an electrostatic field in three dimensions the course of a line of force can be traced out from a given point by first orienting the axes so that x lies along the direction of the electric force at the point, and then continually rotating the axes so that this condition is still obeyed at successive points infinitesimally distant from each other along the curved line which the x -axis thus forms. The properties of the tubes can be expressed in terms of the curvatures of

* Communicated by the Author.

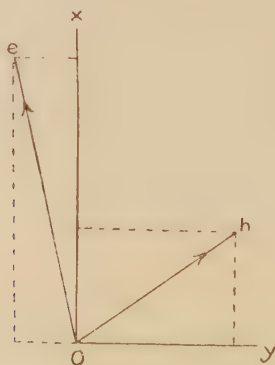
† Proc. Roy. Soc. Edin. xlii. p. 1 (Nov. 1921).

the lines, or in other words in terms of the infinitesimal rotations which are given to the set of axes as the lines are traced out. Although a precisely similar method can be applied to the electromagnetic field, it is not at first sight clear how the axes are to be oriented at any given point which may be chosen as a starting point. In the electromagnetic field the directions of the electric and magnetic forces are in general neither along the same line nor at right angles to each other, and there is no more justification for putting the x -axis along either of these lines than along the other. It is, however, always possible to choose the axes of x , y and z at any point such that their directions enjoy a unique symmetry with respect to \mathbf{e} and \mathbf{h} , in that no predominance is given to either over the other. To effect this choose them so that the following equations are satisfied:—

$$e_z = 0, \quad h_z = 0, \quad e_x e_y + h_x h_y = 0. \quad (1)$$

This makes z perpendicular to the plane in which \mathbf{e} and \mathbf{h} lie at the point, x and y lie in it, their directions, shown in fig. 1, being such as to make the dotted rectangles equal in area.

Fig. 1.



Considering the field as a four-dimensional entity there is the time axis to be oriented also. This lies at right angles to the hyperplane, or instantaneous space in which the axes of x , y and z are drawn. The consideration of the field in hyperspace is greatly simplified by adopting the formal representation of it introduced by Minkowski in which the time axis t is replaced by an "imaginary time" axis $l = ict$, or, taking $c = 1$, $l = it$. The Minkowski world substitutes a

hyperspace with Euclidian geometry in place of the difficult hyperbolic geometry connected with real time. In it \mathbf{e} and \mathbf{h} are vectors which obey at each point (where there is no charge) the formal equivalent of the Maxwellian equations* :

$$\left. \begin{aligned} i \frac{\partial e_x}{\partial l} - \frac{\partial h_z}{\partial y} + \frac{\partial h_y}{\partial z} &= 0, & i \frac{\partial h_x}{\partial l} + \frac{\partial e_z}{\partial y} - \frac{\partial e_y}{\partial z} &= 0, \\ i \frac{\partial e_y}{\partial l} - \frac{\partial h_z}{\partial x} + \frac{\partial h_x}{\partial z} &= 0, & i \frac{\partial h_y}{\partial l} + \frac{\partial e_z}{\partial x} - \frac{\partial e_x}{\partial z} &= 0, \\ i \frac{\partial e_z}{\partial l} - \frac{\partial h_y}{\partial x} + \frac{\partial h_x}{\partial y} &= 0, & i \frac{\partial h_z}{\partial l} + \frac{\partial e_y}{\partial x} - \frac{\partial e_x}{\partial y} &= 0, \\ \frac{\partial e_x}{\partial x} + \frac{\partial e_y}{\partial y} + \frac{\partial e_z}{\partial z} &= 0, & \frac{\partial h_x}{\partial x} + \frac{\partial h_y}{\partial y} + \frac{\partial h_z}{\partial z} &= 0. \end{aligned} \right\} \quad (2)$$

From the point of view of a super-observer surveying the four-dimensional field, or for that matter of a person of ordinary mentality who attempts to form a conception of the underlying reality which shows itself to observers in different hyperplanes as electric and magnetic forces of varying strengths and directions, the hyperplane xyz in which the values of \mathbf{e} and \mathbf{h} are originally specified must be looked upon as an arbitrary one; the l -axis perpendicular to it is therefore also in an arbitrary direction. By means of the Lorentz transformation the hyperplane may be readily changed. If the observer of \mathbf{e} and \mathbf{h} at the point is in motion relatively to it with the velocity v along the axis of z , the observed constitution of the field is changed, and the new electric and magnetic forces are given by the well-known equations

$$\left. \begin{aligned} e'_x &= \beta(e_x - v h_y), & h'_x &= \beta(h_x + v e_y), \\ e'_y &= \beta(e_y + v h_x), & h'_y &= \beta(h_y - v e_x), \\ e'_z &= e_z, & h'_z &= h_z, \end{aligned} \right\} \quad (3)$$

where $\beta = (1 - v^2)^{-\frac{1}{2}}$.

On the Minkowski representation this transformation is

* The mathematical results can always be re-expressed in terms of real time by substituting it for l , $-i \frac{\partial}{\partial t}$ for $\frac{\partial}{\partial l}$.

equivalent to rotating the whole system of axes in the plane of xl through an angle θ given by

$$\tan \theta = iv.$$

If now starting from an arbitrary hyperplane and with the axes of xyz at a given point as origin oriented as in (1), we rotate the axes through the angle θ_{xl} , where

$$\tan \theta_{xl} = i \frac{h_y}{e_x}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

we find for the field as observed in the new hyperplane

$$e'_x = E, \quad e'_y = e'_z = 0, \quad h'_x = H, \quad h'_y = h'_z = 0, \quad . \quad (5)$$

where E and H are related to the usual invariants of the field by the evident relations

$$E^2 - H^2 = e^2 - h^2, \quad EH = (eh). \quad . \quad . \quad . \quad (6)$$

E and H are thus themselves also invariants, and the field at the point has been simplified by the orientation of the axes into a combined electric and magnetic force acting in the same direction along the (unchanged) axis of x^* .

At an infinitesimal distance along the x -axis from the origin e and h will no longer be collinear, but they can be made so again by a suitable orientation of the axes through infinitesimal angles; and it is evident that in this way a continuous line, at every point characterized by the collinearity along it of the transformed electric and magnetic forces, may be constructed in the four-dimensional space. This procedure is precisely analogous to the method of

* When $h_y > e_x$, the transformation (4) involves a velocity greater than that of light for the observer. To get over the difficulty we might use in this case the strictly legitimate transformation

$$\tan \theta_{zl} = i \frac{e_x}{h_y}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

collinearity is again produced, but now along the y -axis. There is, however, no need to deal with it separately, it can be included with the other in the transformation (4) by imagining that the Lorentz equations are valid for values of v greater than 1. It may be noted here that if we apply transformations (4) and (4a) to the same field, while (4) gives collinearity along x with $e'_x = E$, $h'_x = H$, (4a) gives collinearity along y with $e'_y = -iH$, $h'_y = +iE$. It will be evident in § 5 that these are the yz and xl components of the electromagnetic five-vector (R, iR) , and that the two cases consequently form merely different aspects of the same field.

constructing a line of force in an electrostatic field, and the lines so traced out may be called "electromagnetic lines."

Close to the origin the line passing through it lies along the x -direction satisfying equation (1) in the arbitrary hyperplane in which the field is initially specified. This is the case because the rotation of the axes in the plane $z'l$ does not change the axes x and y . Thus the length dx of the line lies in the original hyperplane. For its next infinitesimal portion, however, the rotation to produce collinearity is in general in a plane infinitesimally inclined to the original $z'l$, so that the line bends out of the hyperplane. It is thus in general impossible to draw continuous electromagnetic lines in a fixed hyperplane: at all points, however, the tangents to the lines passing through them may be drawn.

§ 2. Transformation of the Electromagnetic Equations into terms of the Lines.

The axes $xyzl$ having been chosen so that at a given point

$$e_x = E, \quad h_x = H, \quad e_y = e_z = h_y = h_z = 0,$$

at a neighbouring point of the four-dimensional field \mathbf{e} and \mathbf{h} will have the values

$$E + de_x, \quad de_y, \quad de_z, \quad H + dh_x, \quad dh_y, \quad dh_z.$$

We can determine the infinitesimal angles through which the axes have to be rotated to produce collinearity again by the following process. The rotations necessitated by the variations de_y, dh_y are independent of de_x, de_z , etc., and we can treat them as existing separately. Suppose therefore that the new field consists simply of \mathbf{E} and \mathbf{H} along x , and de_y and dh_y along y . Rotate the axes through the angle $d\theta_{xy}$ in the plane of xy until the relation (1) is again obeyed. We shall have for the components of \mathbf{e} and \mathbf{h} along the new axes $x'y'$

$$e_{x'} = E, \quad h_{x'} = H,$$

$$e_{y'} = -E d\theta_{xy} + de_y, \quad h_{y'} = -H d\theta_{xy} + dh_y,$$

and, since they must satisfy the relation

$$e_{x'}e_{y'} + h_{x'}h_{y'} = 0,$$

we have for the angle of rotation

$$d\theta_{xy} = \frac{E de_y + H dh_y}{E^2 + H^2}.$$

Hence

$$e_{y'} = \frac{-H(E dh_y - H de_y)}{E^2 + H^2}, \quad h_{y'} = \frac{E(E dh_y - H de_y)}{E^2 + H^2}.$$

We now further rotate the axes in the plane of $z'l$ (this rotation does not affect directions in the plane xy') through the angle

$$d\theta_{zl} = i \frac{h_{y'}}{e_{y'}} = i \frac{E dh_y - H de_y}{E^2 + H^2}.$$

The axes are now oriented so that \mathbf{e} and \mathbf{h} are collinear, and x lies along the electromagnetic line.

Variations de_z and dh_z are similarly transformed by rotations in the planes of xz and yl through angles

$$d\theta_{xz} = \frac{E de_z + H dh_z}{E^2 + H^2}, \quad d\theta_{yl} = - \frac{iE dh_z - H de_z}{E^2 + H^2}.$$

Variations de_x and dh_x do not involve any rotations of the axes, but we have simply

$$dE = de_x, \quad dH = dh_x.$$

Solving these six equations for de_x , de_y , etc., we obtain

$$\begin{aligned} de_x &= dE, & dh_x &= dH, \\ de_y &= E d\theta_{xy} + iH d\theta_{zl}, & dh_y &= H d\theta_{xy} - iE d\theta_{zl}, \\ de_z &= E d\theta_{xz} - iH d\theta_{yl}, & dh_z &= H d\theta_{xz} + iE d\theta_{yl}. \end{aligned} \quad (7)$$

These form a set of transformation equations by which we can express the infinitesimal variations of \mathbf{e} and \mathbf{h} between the origin and a neighbouring point in terms of the collinear invariants E and H and of the infinitesimal angles through which the system of axes has to be rotated in order to lay the axes at the neighbouring point along the appropriate directions for observing the collinearity.

Let the values (7) be substituted in the electromagnetic equations (2); if we multiply the resulting equations by E and H , add or subtract them in suitable pairs, and observe that the sign of θ is reversed by changing the order of its suffixes, we get the following set of eight equations which

forms a complete equivalent of the original set (2) :

$$\left. \begin{aligned}
 E \frac{\partial E}{\partial x} + H \frac{\partial H}{\partial x} + (E^2 + H^2) \left(\frac{\partial \theta_{xy}}{\partial y} + \frac{\partial \theta_{xz}}{\partial z} \right) &= 0, \dots (a) \\
 E \frac{\partial E}{\partial y} + H \frac{\partial H}{\partial y} + (E^2 + H^2) \left(\frac{\partial \theta_{ly}}{\partial y} + \frac{\partial \theta_{lz}}{\partial z} \right) &= 0, \dots (b) \\
 E \frac{\partial E}{\partial x} + H \frac{\partial H}{\partial x} + (E^2 + H^2) \left(\frac{\partial \theta_{yx}}{\partial x} + \frac{\partial \theta_{yl}}{\partial l} \right) &= 0, \dots (c) \\
 E \frac{\partial E}{\partial z} + H \frac{\partial H}{\partial z} + (E^2 + H^2) \left(\frac{\partial \theta_{zx}}{\partial x} + \frac{\partial \theta_{zl}}{\partial l} \right) &= 0, \dots (d) \\
 E \frac{\partial H}{\partial x} - H \frac{\partial E}{\partial x} + i(E^2 + H^2) \left(\frac{\partial \theta_{lx}}{\partial y} + \frac{\partial \theta_{yl}}{\partial z} \right) &= 0, \dots (a') \\
 E \frac{\partial H}{\partial y} - H \frac{\partial E}{\partial y} + i(E^2 + H^2) \left(\frac{\partial \theta_{yx}}{\partial y} + \frac{\partial \theta_{yz}}{\partial z} \right) &= 0, \dots (b') \\
 E \frac{\partial H}{\partial x} - H \frac{\partial E}{\partial x} + i(E^2 + H^2) \left(\frac{\partial \theta_{xl}}{\partial x} + \frac{\partial \theta_{xz}}{\partial l} \right) &= 0, \dots (c') \\
 E \frac{\partial H}{\partial z} - H \frac{\partial E}{\partial z} + i(E^2 + H^2) \left(\frac{\partial \theta_{ly}}{\partial x} + \frac{\partial \theta_{lx}}{\partial l} \right) &= 0, \dots (d')
 \end{aligned} \right\} (8)$$

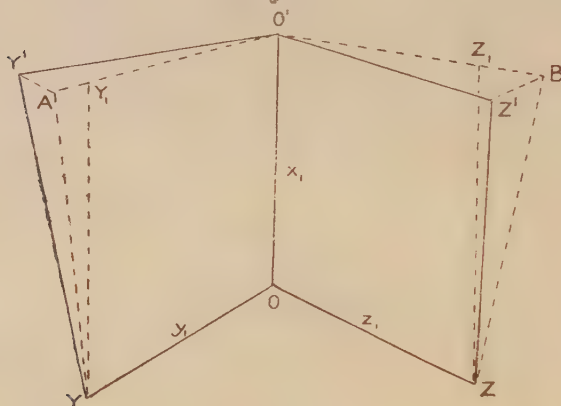
§ 3. A Flux Theorem for each of four Electromagnetic Tubes.

To interpret the equations (8) we observe that through any point of the four-dimensional field not one only but *four* electromagnetic lines may be constructed, each of which is uniquely determined when the initial hyperplane in which the field is specified is given. Starting from this hyperplane the four axes' directions required to produce collinearity at a given point are uniquely fixed. We can thus proceed to a neighbouring point lying on any of these axes, and rotate the system to give collinearity at this point, and by continuing this process obtain a continuous curved line in hyperspace which at the origin coincides with the given axis. We will call these curved lines the x, y, z, l -electromagnetic lines respectively; bounded by a set of each of them an x, y, z, l -electromagnetic tube can be constructed in the usual way.

Consider now an infinitely thin x -tube, which we may take as having a rectangular cross-section at the origin.

Let the adjacent edges of the section which contain the origin be infinitesimal lengths $OY=y_1$, $OZ=z_1$ (fig. 2) of the y and z -lines through the origin respectively, and let YY' , ZZ' be the x -lines through Y and Z . The area of the

Fig. 2.



section at the origin is $y_1 z_1$. The cross-section at an infinitesimal distance along the x -line of $OO'=x_1$ will be a quadrilateral whose sides are

$$O'Y' = y_1 + x_1 \frac{\partial y_1}{\partial x}, \quad O'Z' = z_1 + x_1 \frac{\partial z_1}{\partial x},$$

and which will be altered in size, shape, and orientation from the original rectangle. If Y_1 and Z_1 are the projections of Y and Z by lines parallel to OO' , and we draw $Y'A$, $Z'B$ perpendicular to $O'Y_1$ and $O'Z_1$, we can readily see that

$$\frac{\partial \theta_{xy}}{\partial y} = \frac{\angle Y_1YA}{y_1} = \frac{1}{y_1} \cdot \frac{Y_1A}{x_1} = \frac{1}{y_1} \frac{\partial y_1}{\partial x},$$

and similarly

$$\frac{\partial \theta_{xz}}{\partial z} = \frac{1}{z_1} \frac{\partial z_1}{\partial x}.$$

On substituting these in (8a) that equation becomes

$$E \frac{\partial E}{\partial x} + H \frac{\partial H}{\partial x} + (E^2 + H^2) \frac{1}{y_1 z_1} \frac{\partial}{\partial x} (y_1 z_1) = 0$$

or

$$\frac{\partial}{\partial x} (\sqrt{E^2 + H^2} \cdot y_1 z_1) = 0. \quad \dots \quad (9a)$$

This equation expresses the fact that the flux of the invariant function $\sqrt{E^2 + H^2}$ over the cross-section $y_1 z_1$ of an infinitely thin x -tube is constant throughout the whole tube; since any tube may be formed by the juxtaposition of infinitely thin elementary tubes, the statement is true for a tube of finite cross-section also. In this case the corresponding cross-section may be defined as any continuous surface at any point of which the yz plane corresponding to the x -line passing through the point differs only infinitesimally from being tangential*.

On the rectangle $y_1 z_1$ as base not only an x -tube but also an l -tube may be constructed, since the l - as well as the x -lines are at right angles to yz . The same figure 2 with OO' representing the l -axis gives

$$\frac{\partial \theta_{ly}}{\partial y} = \frac{1}{y_1} \frac{\partial y_1}{\partial l}, \quad \frac{\partial \theta_{lz}}{\partial z} = \frac{1}{z_1} \frac{\partial z_1}{\partial l},$$

and equation (8b) reduces to

$$\frac{\partial}{\partial l} (\sqrt{E^2 + H^2} \cdot y_1 z_1) = 0, \quad \dots \quad (9b)$$

so that the flux theorem applies to the l -tube also.

Any infinitely thin tube constructed of either y - or z -lines will at the origin be perpendicular to the plane xl . Take the cross-section at the origin to be rectangular, formed of infinitely short x - and l -lines, x_1 and l_1 . We find as before

$$\begin{aligned} \frac{\partial \theta_{yx}}{\partial x} &= \frac{1}{x_1} \frac{\partial x_1}{\partial y}, & \frac{\partial \theta_{yl}}{\partial l} &= \frac{1}{l_1} \frac{\partial l_1}{\partial y}, \\ \frac{\partial \theta_{zx}}{\partial x} &= \frac{1}{x_1} \frac{\partial x_1}{\partial z}, & \frac{\partial \theta_{zl}}{\partial l} &= \frac{1}{l_1} \frac{\partial l_1}{\partial z}. \end{aligned}$$

* In the general field the x -lines are twisted in the yz plane (*v. infra*) and a closed surface everywhere perpendicular to them cannot be uniquely constructed; *i. e.*, if we go from the origin always perpendicular to the x -lines distances, first y_1 and then z_1 , we do not arrive at the same point of the final x -line as will be reached by going the same distances in the opposite order, mathematically the conditions of unconditional integrability will not be satisfied for the y_1 and z_1 displacements. For the purpose of reckoning the flux this feature of the tubes is immaterial, all the surfaces formed by joining up the points obtained by displacements in any order will over an infinitesimal region only differ from each other in area by second order quantities. The curvatures of the x -lines, and the second order displacements which they have undergone at O' , Y and Z out of the hyperplane xyz , are also of negligible effect.

With these substitutions (8 c) and (8 d) become

$$\frac{\partial}{\partial y} (\sqrt{E^2 + H^2} \cdot x_1 l_1) = 0, \quad . \quad . \quad . \quad (9 c)$$

$$\frac{\partial}{\partial z} (\sqrt{E^2 + H^2} \cdot x_1 l_1) = 0. \quad . \quad . \quad . \quad (9 d)$$

It thus appears that a theorem expressing the constancy of the flux over the cross-section of the tube is derivable for each one of the four electromagnetic tubes which can be constructed with any point of the field as origin. The cross-section over which the flux is reckoned is determined by the particular hyperplane which contains the infinitesimal portion of the tube concerned. The x - and l -tubes lie initially in the hyperplanes xyz , lyz respectively, and have the same cross-section $y_1 z_1$; the y - and z -tubes lie in pxl , zxl , and have the same cross-section $x_1 l_1$. The same quantity $\sqrt{E^2 + H^2}$ appears in each case as the function whose flux is constant; it will be convenient to represent it by a single symbol R . In terms of the invariants of the field as usually expressed we have by (6) .

$$\begin{aligned} R &= \sqrt{E^2 + H^2} = \{ (E^2 - H^2)^2 + 4E^2 H^2 \}^{\frac{1}{4}} \\ &= \{ (\mathbf{e}^2 - \mathbf{h}^2)^2 + 4(\mathbf{eh})^2 \}^{\frac{1}{4}}. \quad . \quad . \quad (10) \end{aligned}$$

In the special case when \mathbf{e} and \mathbf{h} are everywhere at right angles to each other $(\mathbf{eh}) = 0$ and

$$R = \sqrt{\mathbf{e}^2 - \mathbf{h}^2}.$$

This is a result which has already been given in Prof. Whitaker's paper. The Lorentz transformation also shows that when \mathbf{e} and \mathbf{h} are perpendicular, $H = 0$ and $R = E$, hence when they are viewed at any point in the appropriate hyperplane the electromagnetic x -lines are lines of pure electric force, they may however differ from ordinary electrostatic lines by their whole lengths not being containable in a single hyperplane.

§ 4. *A Theorem, complementary to the preceding, relating to the Twist of each Tube.*

The expression of the constancy of the flux of R for the four tubes only accounts for half the information derivable from the eight electromagnetic equations. The second four of the equations in (8) are concerned with what we may call

the "internal composition" of the vector R . An electrostatic tube in three-dimensional space is characterized by only two quantities at each point: its direction, and the electric force e which is inversely proportional to its sectional area at the point. An electromagnetic tube in hyperspace has not two but three such characteristic quantities. Not only will the same tube in two different places differ in direction, and in the magnitude of the vector function of position R , which latter is inversely proportional to the sectional area of the tube, but $R = \sqrt{E^2 + H^2}$ will differ in the relative proportions of the collinear E and H of which it is composed. The composition of R is adequately expressed by a parameter α such that

$$\sin \alpha = \frac{H}{\sqrt{E^2 + H^2}} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$\sin \alpha$ measures at any point the relative amount of magnetic force in R which cannot possibly be transformed away. We have further from (6)

$$\sin 2\alpha = \frac{2EH}{E^2 + H^2} = \frac{2(eh)}{R^2}.$$

Thus also $\sin 2\alpha$ gives a direct measure at each point of the departure of the field from orthogonality of e and h , as expressed by the value relative to R^2 of the scalar-product invariant $2(eh)$.

Differentiating (11) we have

$$EdH - HdE = R^2 d\alpha,$$

the substitution of which in (8 $a'-d'$) gives

$$\left. \begin{aligned} \frac{\partial \alpha}{\partial x} + i \left(\frac{\partial \theta_{lx}}{\partial y} + \frac{\partial \theta_{ly}}{\partial z} \right) &= 0, \\ \frac{\partial \alpha}{\partial l} + i \left(\frac{\partial \theta_{zx}}{\partial y} + \frac{\partial \theta_{xy}}{\partial z} \right) &= 0, \\ \frac{\partial \alpha}{\partial y} + i \left(\frac{\partial \theta_{xl}}{\partial x} + \frac{\partial \theta_{xz}}{\partial l} \right) &= 0, \\ \frac{\partial \alpha}{\partial z} + i \left(\frac{\partial \theta_{ly}}{\partial x} + \frac{\partial \theta_{yx}}{\partial l} \right) &= 0. \end{aligned} \right\} \quad . \quad . \quad . \quad (12)$$

These equations disclose that the variation of α in each of the four coordinate directions is determined by the extent to

which twisting occurs in a corresponding tube. In a twisted tube the bounding lines will not be parallel to the tube axis but will tend to run in spiral curves around it. Fig. 2 (p. 712) shows the effect of a twist on the x -tube. Let $x_1 \frac{\partial \phi_{zy}'}{\partial x}$, $x_1 \frac{\partial \phi_{zy}''}{\partial x}$ be the angles $Y'O'Y_1$, $Z'O'Z_1$ through which $O'Y'$, $O'Z'$ have been rotated from OY , OZ in the plane yz , while $Y'YA$, $Z'ZB$ are the angles $y_1 \frac{\partial \theta_{zx}}{\partial y}$, $z_1 \frac{\partial \theta_{xy}}{\partial z}$ through which the x -lines through Y and Z have been rotated in the planes zx , xy respectively from the x -line through O . We see at once by expressing AY' , BZ' in terms of these that

$$\frac{\partial \theta_{zx}}{\partial y} = \frac{\partial \phi_{zy}'}{\partial x}, \quad \frac{\partial \theta_{xy}}{\partial z} = \frac{\partial \phi_{zy}''}{\partial x} \quad \dots \quad (13)$$

When $Y'O'Y_1$, $Z'O'Z_1$ are not equal there is distortion as well as twist; the two may be separated in the usual way by writing

$$\left. \begin{aligned} \phi_{yz} &= -\psi_{yz} = -\frac{1}{2}(\phi_{zy}' + \phi_{zy}''), \\ \psi_{yz} &= -\phi_{yz} = -\frac{1}{2}(\phi_{zy}' - \phi_{zy}''), \end{aligned} \right\} \quad \dots \quad (14)$$

$\frac{\partial \phi_{yz}}{\partial x}$ measures the pure twist, or the rate at which the rectangle $y_1 z_1$ is undergoing rotation in its own plane in the direction from y to z as we proceed along the x -tube, while $\frac{\partial \psi_{yz}}{\partial x}$ expresses the rate at which it undergoes distortion. These considerations are applicable to any tube. For the x - and l -tubes erected on the same base $y_1 z_1$, $\frac{\partial \phi_{yz}}{\partial x}$, $\frac{\partial \phi_{yz}}{\partial l}$ represent the respective twists. The y - and z -tubes, based on $x_1 l_1$, are twisted in the xl plane: let $\frac{\partial \phi_{xl}}{\partial y}$, $\frac{\partial \phi_{xl}}{\partial z}$ be their respective twists. We then have from (13) and (14), and corresponding formulæ for the other tubes

$$\begin{aligned} \frac{\partial \theta_{lz}}{\partial y} + \frac{\partial \theta_{yl}}{\partial z} &= +2 \frac{\partial \phi_{yz}}{\partial l}, & \frac{\partial \theta_{zl}}{\partial x} + \frac{\partial \theta_{xz}}{\partial l} &= +2 \frac{\partial \phi_{xl}}{\partial z}, \\ \frac{\partial \theta_{zx}}{\partial y} + \frac{\partial \theta_{xy}}{\partial z} &= -2 \frac{\partial \phi_{yz}}{\partial x}, & \frac{\partial \theta_{ly}}{\partial x} + \frac{\partial \theta_{yx}}{\partial l} &= -2 \frac{\partial \phi_{xl}}{\partial y}, \end{aligned}$$

and equations (12) become

$$\left. \begin{aligned} \frac{\partial \alpha}{\partial x} &= -2i \frac{\partial \phi_{yz}}{\partial l}, & \frac{\partial \alpha}{\partial y} &= -2i \frac{\partial \phi_{xl}}{\partial z}, \\ \frac{\partial \alpha}{\partial l} &= +2i \frac{\partial \phi_{yz}}{\partial x}, & \frac{\partial \alpha}{\partial z} &= +2i \frac{\partial \phi_{xl}}{\partial y}. \end{aligned} \right\} \quad (15)$$

These equations, one for each tube, are complementary to the corresponding equations expressing the flux theorems, and show that the tubes give a complete representation of the electromagnetic field. Equations (9) show that the tubes, by the variation of their cross-sections, determine the variations of R , equations (15) show that by their twists, they determine the variations of α , along each of the four coordinate directions. It should be noted, however, that while the variation of R given by each tube— x, l, y, z —is that along the length of the tube, the variation of α given by the twist is along a direction perpendicular to the tube, but specially associated with it,— l, x, z, y .

§ 5. An Electromagnetic Fire-Vector characteristic of the Field.

The meaning of these results can be made clearer by observing that the geometrical construction by which the electromagnetic lines passing through a given point have been obtained still leaves their directions in hyperspace subject to a certain amount of arbitrariness. They are only uniquely fixed when the arbitrary initial hyperplane is given (*cf.* § 3). In fact the final directions of the lines can be got from an arbitrary initial set of axes by four successive rotations in the planes of xy, xz, yl , and zl , and rotations in the planes xl and yz are not required to produce collinearity of \mathbf{e} and \mathbf{h} . They may be made of course, but they do not affect the collinearity. Thus in a hyperplane in which collinearity is observed at a given point, let the observer suppose that he is in motion with a velocity v along the x -axis, *i. e.* along the direction of \mathbf{E} and \mathbf{H} . The Lorentz transformation shows that this will affect in no way the magnitudes of \mathbf{E} and \mathbf{H} at the point; it follows, therefore, that the observer has no means of ascertaining his velocity in this direction, or of concluding that he has none, by observation of the field at this single point. We have therefore no right to assume that this velocity is zero, but in a general theory should write it as an arbitrarily given quantity. The corresponding transformation is equivalent to rotating the axes through an arbitrary angle in the plane of xl , and thus to

laying down in hyperspace $x'l$ - and $l'l$ -lines in a different direction from before, although still in the unaltered xl plane. Similar considerations apply to the y and z axes; indeed, when collinearity of \mathbf{e} and \mathbf{h} has been obtained it is evident that there is nothing to distinguish their actual directions in the fixed plane yz .

It thus appears that what is uniquely fixed in hyperspace is not the directions of the individual axes, but the orientations at the point of the two coordinate planes xl and yz , in which planes the axes themselves may be drawn arbitrarily. The entity that we have really to deal with in a four-dimensional theory of the electromagnetic field is of the type which is best represented not by lines but by surfaces: in other words, it is not of the four-vector, but of the six-vector type, being a function of position the properties of which at any point are associated with two absolutely orthogonal planes (xl and yz) which cut each other only at that point*. The six-vector in question is of a restricted type, characterized by the equality of its two parts; it consists of $\mathbf{R} = \sqrt{\mathbf{E}^2 + \mathbf{H}^2}$ associated with the yz plane by "acting" in any direction perpendicular to it, *i. e.*, along any line in the plane xl , combined with the equal (but imaginary) quantity $i\mathbf{R}$ similarly associated with the xl plane. Although a six-vector, since its two parts are equal, it only requires five independent quantities to specify it: the four quantities required to fix the orientations of the planes, along with the magnitude of \mathbf{R} . We will call it consequently a "five-vector," thereby distinguishing it from the electromagnetic six-vector ($\mathbf{h} - i\mathbf{e}$). The six quantities required to specify completely the field at a point are known when α is given in addition.

§ 6. *The Construction of Unique Sets of Tubes.*

These considerations enable us to explain the special symmetry which the tubes show in the planes xl and yz , and at the same time to derive a set of tubes which are really uniquely laid down in hyperspace. Having obtained from any initial hyperplane the axes oriented so that x lies along the collinear \mathbf{E} and \mathbf{H} , let the axes be further rotated through the angle θ_{xl} in the plane xl . This will not affect \mathbf{E} , \mathbf{H} , or the axes y , z . Starting from the origin along the new direction x' of x , we can construct an x' -line just as before by

* The plane xl comprises all points of hyperspace for which $y=0$, $z=0$; yz all points for which $x=0$, $l=0$; the two planes thus cut only at the origin.

infinitesimal rotations in the planes $x'y$, $x'z$, $y'l$, $z'l$ alone. For the corresponding x' -tube we shall have

$$\begin{aligned} \frac{\partial}{\partial x'}(\sqrt{E^2+H^2} \cdot y_1 z_1) \\ = \left(\cos \theta_{xl} \cdot \frac{\partial}{\partial x} + \sin \theta_{xl} \cdot \frac{\partial}{\partial l} \right) (\sqrt{E^2+H^2} \cdot y_1 z_1) \\ = 0 \quad \text{by (9 a, b).} \end{aligned}$$

Hence the flux theorem applies to a tube starting from the origin in any direction in the plane of xl , the properties of the x - and l -tubes are in fact symmetrical in this plane. Since θ_{xl} is arbitrary, we may choose it so as to satisfy any stated condition, for example, the condition that

$$\frac{\partial \alpha}{\partial x'} = \cos \theta_{xl} \frac{\partial \alpha}{\partial x} + \sin \theta_{xl} \frac{\partial \alpha}{\partial l} = 0.$$

It is clear that in this way an x' -line may be drawn such that there is no change in the composition of R along it, and it is now also uniquely laid down in hyperspace. When

$\frac{\partial \alpha}{\partial x'} = 0$, (15) shows that $\frac{\partial \phi_{yz}}{\partial l'^2} = 0$, which means that there

is no twist round the l' direction perpendicular to x' . Hence the "twist of the xl plane," *i. e.* the twist round its axis of any infinitely thin tube drawn in it, is a maximum round the particular x' -line which does not vary in composition along its length, while the l' -line at right angles to x' is characterized by no twist round it, and along it a maximum rate of change of composition. In fact, in the xl plane (and all these conclusions apply also to the plane yz) the vectors representing the twist and the gradient of α are in mutually perpendicular directions*.

* Some sort of a visualization of the effects of twist can be got by picturing an x -line as being something like a ribbon instead of being the same all round like an ordinary line. We can suppose it shows E on the face and H on the edge of the ribbon. The Lorentz transformation enables one to alter the view point, and with untwisted ribbons to change the \mathbf{h} -aspect of the field completely into \mathbf{e} ; when they are twisted however it is impossible to find any view point from which the \mathbf{e} - or the \mathbf{h} -aspect alone may be seen; they must both show simultaneously. This agrees with what has been deduced: when \mathbf{e} and \mathbf{h} are perpendicular, one of them may be transformed away, when they are not perpendicular the lines are twisted and neither can be transformed away completely. It also enables us to visualize how twisted tubes might produce space-time variations in the ratio of H to E . It is, however, only a crude analogy and must not be pushed too far. As a fact the composition of the lines changes in a direction perpendicular to the axis of twist, and not along it as the analogy would suggest.

Summary.

When viewed in a suitable hyperplane, *i. e.*, when suitably transformed, the electric and magnetic forces at any point of the general electromagnetic field can be made to coincide in direction. This direction determines an electromagnetic line, continuous through hyperspace, from a set of which an electromagnetic tube can be constructed. Four such tubes, mutually perpendicular, can be constructed containing any point, and each is characterized by the constancy of the flux of the quantity

$$R = \{(e^2 - h^2)^2 + 4(eh)^2\}^{\frac{1}{4}}$$

over its cross section. A complementary theorem for each tube relating to the twist of its generating lines determines the internal constitution of R as expressed by the ratio of the magnetic to the electric force present in the compound vector. R is shown to be a "five-vector," *i. e.*, a six-vector with its two parts equal; it is a function of position associated with two absolutely orthogonal planes uniquely fixed at each point of the four-dimensional field.

The University, Sheffield,
29th June, 1922.

LXII. *Radiation.* By ARTHUR BRAMLEY.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN the following discussion we shall make use of the idea that energy possesses mass, a principle which has been so fruitful in explaining the behaviour of light-rays in a gravitational field and which is a natural consequence of the electromagnetic theory.

If energy possesses mass, then the fundamental laws of mechanics ought to apply to it. Following this idea, we shall attempt to show how the laws of radiation are related to the fundamental principles of mechanics and electrodynamics.

The values of the potentials are :

$$\nabla^2 \phi - \frac{1}{c^2} \frac{\partial^2 \phi}{\partial t^2} = -\rho,$$

$$\nabla^2 U - \frac{1}{c^2} \frac{\partial^2 U}{\partial t^2} = -\rho \frac{V}{c},$$

$$E = -\frac{1}{c} \frac{\partial U}{\partial t} - \text{grad } \phi,$$

$$H = \text{rot } U.$$

We shall suppose that the charged system is rotating in the XY plane around the origin as centre with uniform circular motion. Transforming to coordinates moving with the charge we have $x = r \cos \omega t$, $y = r \sin \omega t$, or calling $\omega t = \theta$ we have

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2}.$$

But
$$\frac{\partial^2}{\partial t^2} = \omega^2 \frac{\partial^2}{\partial \theta^2},$$

then
$$\frac{\partial^2 \phi}{\partial r^2} + \frac{1}{r} \frac{\partial \phi}{\partial r} + \frac{\partial^2 \phi}{\partial z^2} + \left(\frac{1}{r^2} - \frac{\omega^2}{c^2} \right) \frac{\partial^2 \phi}{\partial \theta^2} = -\rho,$$

or
$$\frac{\partial^2 \phi}{\partial r^2} + \frac{1}{r} \frac{\partial \phi}{\partial r} + \frac{\partial^2 \phi}{\partial z^2} + \frac{1}{r^2} (1 - \beta^2) \frac{\partial^2 \phi}{\partial \theta^2} = -\rho.$$

Now let $\theta_1 = \theta / \sqrt{1 - \beta^2},$

we have
$$\frac{\partial^2 \phi}{\partial r^2} + \frac{1}{r} \frac{\partial \phi}{\partial r} + \frac{\partial^2 \phi}{\partial z^2} + \frac{1}{r^2} \frac{\partial^2 \phi}{\partial \theta_1^2} = -\rho,$$

since the terms involving the velocities are negligible in comparison with the other terms.

Now
$$\frac{\partial}{\partial t} = \frac{\partial}{\partial \theta} \cdot \frac{\partial \theta}{\partial t} = \frac{\partial}{\partial \theta} \left(\omega + t \frac{\partial \omega}{\partial t} \right) = \frac{\partial}{\partial \theta} \left(1 + t \frac{\partial}{\partial t} \right) \omega,$$

$$\frac{\partial^2}{\partial t^2} = \frac{\partial^2}{\partial \theta^2} \left(1 + t \frac{\partial}{\partial t} \right)^2 \omega^2 + \frac{\partial}{\partial \theta} \left(2 \frac{\partial \omega}{\partial t} + t \frac{\partial^2 \omega}{\partial t^2} \right),$$

or
$$\frac{\partial^2}{\partial t^2} = \frac{\partial^2}{\partial \theta^2} \left(1 + t \frac{\partial}{\partial t} \right)^2 \omega^2.$$

If
$$2 \frac{\partial \omega}{\partial t} + t \frac{\partial^2 \omega}{\partial t^2} = 0,$$

or
$$\frac{\partial \omega}{\partial t} = kt^{-2},$$

which is very probably the case for small oscillations

then
$$\omega + t \frac{\partial \omega}{\partial t} = \omega + kt^{-1}.$$

But the time during which the electron is oscillating is so great that $kt^{-1} \ll \omega$,

or
$$\frac{\partial^2}{\partial t^2} = \omega^2 \frac{\partial^2}{\partial \theta^2}.$$

Also

$$\begin{aligned}\nabla_1^2 U &= -\beta \rho, \\ \rho r d\theta dr dz &= \rho_1 r d\theta_1 dr dz, \\ d\theta &= d\theta_1 \sqrt{1-\beta^2}, \\ d\tau &= d\tau_1 \sqrt{1-\beta^2},\end{aligned}$$

or

$$\rho_1 = \rho \sqrt{1-\beta^2};$$

$$\therefore \nabla_1^2 \phi_1 = -\rho_1 = -\sqrt{1-\beta^2} \cdot \rho.$$

But ϕ satisfies

$$\nabla_1^2 \phi = -\rho;$$

$$\therefore \phi_1 = \sqrt{1-\beta^2} \cdot \phi.$$

Assuming that $\frac{dr}{dt} < 1$, and using Boussinesq's definition of an harmonic,

$$\begin{aligned}\frac{\partial \phi}{\partial r} &= \frac{1}{\sqrt{1-\beta^2}} \cdot \frac{\partial \phi_1}{\partial r}, \\ \frac{\partial \phi}{\partial z} &= \frac{1}{\sqrt{1-\beta^2}} \cdot \frac{\partial \phi_1}{\partial z}, \\ \frac{\partial \phi}{\partial \theta} &= \frac{1}{\sqrt{1-\beta^2}} \cdot \frac{\partial \phi}{\partial \theta_1} = \frac{1}{1-\beta^2} \cdot \frac{\partial \phi_1}{\partial \theta_1}.\end{aligned}$$

Moreover,

$$U_\theta = \beta \phi, \quad U_r = U_z = 0.$$

Now

$$E_z = -\frac{1}{\sqrt{1-\beta^2}} \cdot \frac{\partial \phi_1}{\partial z},$$

$$E_r = -\frac{1}{\sqrt{1-\beta^2}} \cdot \frac{\partial \phi_1}{\partial r},$$

$$E_\theta = -\frac{1}{c} \frac{\partial}{\partial t} (U_\theta) - \frac{1}{r} \frac{\partial \phi}{\partial \theta},$$

$$= -\frac{1}{c} \frac{\partial}{\partial t} (\beta \phi) - \frac{1}{r} \frac{\partial \phi}{\partial \theta},$$

$$= -\frac{\dot{\beta}}{c^2} \phi - \left(\frac{\beta \omega}{c} + \frac{1}{r} \right) \frac{\partial \phi}{\partial \theta},$$

$$= -\frac{\dot{\beta}}{c^2} \frac{\phi_1}{\sqrt{1-\beta^2}} - \frac{1}{r} \left\{ \frac{1+\beta^2}{1-\beta^2} \right\} \frac{\partial \phi_1}{\partial \theta_1}.$$

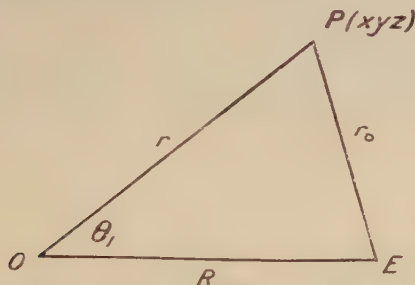
Further

$$H_z = \frac{1}{r} \frac{\partial U_r}{\partial \theta} - \frac{\partial U_\theta}{\partial r} = -\beta \frac{\partial \phi}{\partial r} = -\frac{\beta}{\sqrt{1-\beta^2}} \cdot \frac{\partial \phi_1}{\partial r},$$

$$H_\theta = \frac{\partial U_z}{\partial r} - \frac{\partial U_r}{\partial z} = 0,$$

$$\begin{aligned}
 H_r &= \frac{\partial U_\theta}{\partial z} - \frac{1}{r} \frac{\partial U_z}{\partial \theta} = \beta \frac{\partial \phi}{\partial z} - \frac{1}{r} \frac{\partial \beta}{\partial \theta} \cdot \phi, \\
 &= \frac{\beta}{\sqrt{1-\beta^2}} \frac{\partial \phi_1}{\partial z} - \frac{1}{r\omega} \cdot \frac{\phi_1}{\sqrt{1-\beta^2}} \cdot \frac{\partial \beta}{\partial \theta}, \\
 &= \frac{\beta}{\sqrt{1-\beta^2}} \frac{\partial \phi_1}{\partial z} - \frac{1}{uc} \cdot \frac{\phi_1 u}{\sqrt{1-\beta^2}}.
 \end{aligned}$$

Now for the contractile electron the potential ϕ_1 is symmetrical in the distorted space of the fixed system and equal to $\frac{e}{4\pi r_1}$ where r_1 is the distance from the centre of the sphere in this system.



Let $P(xyz)$ be a point in space in the XY plane, r_0 the projection of r_1 on that plane, and θ_1 the angle POE where E is the position of the electron whose orbital radius is R .

Then we have

$$\begin{aligned}
 r_1^2 &= r_0^2 + z^2; \\
 r_0^2 &= r_1^2 - z^2, \\
 r_0^2 &= r^2 + R^2 - 2rR \cos \theta_1, \\
 r_1^2 &= r^2 + R^2 + z^2 - 2rR \cos \theta_1.
 \end{aligned}$$

Therefore

$$r_1 = (r^2 + R^2 + z^2 - 2rR \cos \theta_1)^{1/2},$$

which gives $\phi_1 = \frac{e}{4\pi} \cdot \frac{1}{\sqrt{r^2 + R^2 + z^2 - 2rR \cos \theta_1}}.$

Whence we have

$$\begin{aligned}
 \frac{\partial \phi_1}{\partial z} &= \frac{-z}{(r^2 + R^2 - 2rR \cos \theta_1 + z^2)^{3/2}} \cdot \frac{e}{4\pi}, \\
 \frac{\partial \phi_1}{\partial r} &= \frac{-r + R \cos \theta_1}{(r^2 + R^2 - 2rR \cos \theta_1 + z^2)^{3/2}} \cdot \frac{e}{4\pi}, \\
 \frac{\partial \phi_1}{\partial \theta_1} &= \frac{-rR \sin \theta_1}{(r^2 + R^2 - 2rR \cos \theta_1 + z^2)^{3/2}} \cdot \frac{e}{4\pi}.
 \end{aligned}$$

Then

$$E_R = \frac{e}{4\pi} \cdot \frac{1}{\sqrt{1-\beta^2}} \cdot \frac{r - R \cos \theta_1}{(r^2 + R^2 + z^2 - 2rR \cos \theta_1)^{3/2}},$$

$$E_z = \frac{e}{4\pi} \cdot \frac{1}{\sqrt{1-\beta^2}} \cdot \frac{z}{(r^2 + R^2 + z^2 - 2rR \cos \theta_1)^{3/2}},$$

$$E_\theta = \frac{e}{4\pi} \cdot \frac{-\dot{u}}{c^2} \cdot \frac{1}{\sqrt{1-\beta^2}} \cdot \frac{1}{(r^2 + R^2 + z^2 - 2rR \cos \theta_1)^{1/2}} \\ + \frac{1+\beta^2}{1-\beta^2} \cdot \frac{e}{4\pi} \cdot \frac{R \sin \theta_1}{(r^2 + R^2 + z^2 - 2rR \cos \theta_1)^{3/2}};$$

and $H_\theta = 0$,

$$H_z = \frac{e}{4\pi} \cdot \frac{\beta}{\sqrt{1-\beta^2}} \cdot \frac{r - R \cos \theta_1}{(r^2 + R^2 + z^2 - 2rR \cos \theta_1)^{3/2}},$$

$$H_R = \frac{e}{4\pi} \cdot \frac{\beta}{\sqrt{1-\beta^2}} \cdot \frac{-z}{(r^2 + R^2 + z^2 - 2rR \cos \theta_1)^{3/2}} \\ - \frac{e}{4\pi} \cdot \frac{\dot{u}}{uc} \cdot \frac{1}{\sqrt{1-\beta^2}} \cdot \frac{1}{(r^2 + R^2 + z^2 - 2rR \cos \theta_1)^{1/2}},$$

where $r_1 = (r^2 + R^2 + z^2 - 2rR \cos \theta_1)^{1/2}$ = distance from the electron's centre to the point in question.

The calculated values of H and E along the axis of revolution agree with those found by other means except for the terms involving the accelerations.

It will be observed that this part of the force varies inversely as the square of the distance of the point from the moving charge, and is therefore inappreciable at great distances.

Turning to the part of the intensities which involves the accelerations we have two components,

$$E_\theta = \frac{e}{4\pi} \cdot \frac{-\dot{u}}{c^2} \cdot \frac{1}{\sqrt{1-\beta^2}} \cdot \frac{1}{(r^2 + R^2 + z^2 - 2rR \cos \theta_1)^{1/2}},$$

$$H_R = \frac{e}{4\pi} \cdot \frac{-\dot{u}}{uc} \cdot \frac{1}{\sqrt{1-\beta^2}} \cdot \frac{1}{(r^2 + R^2 + z^2 - 2rR \cos \theta_1)^{1/2}}.$$

Thus we see that the part of the electromagnetic field which depends on the acceleration of the particle is specified by two vectors, the electric and magnetic intensities. These are mutually perpendicular but not equal in magnitude, except for the special case that $u=c$. There is another important difference between the part of the field which depends on the acceleration and that which does not; in the

latter the intensities are both inversely proportional to the square of the distance, while in the former they are inversely as the first power, so that at great distances from the moving charge the part of the field which depends on the acceleration will become very great in comparison with the other part.

The energy of the field is :

$$u = \frac{1}{2} \{ H^2 + E^2 + 2(HH_1) + 2(EE_1) + H_1^2 + E_1^2 \},$$

where the terms with suffixes depend on the acceleration.

We shall consider the latter part only.

Since the energy per unit volume is $\frac{1}{2}(E_1^2 + H_1^2)$ we have for the volume density $\frac{1}{2}E_1^2 \left(1 + \frac{u^2}{c^2}\right)$ for $E_1 = H_1 \cdot \frac{u}{c}$.

The stream of energy passing any point per unit of area is equal to $c[E \cdot H]$, the direction of the stream being along the perpendicular to the plane of the orbit.

Now

$$c[E \cdot H] = \frac{e^2}{16\pi^2} \cdot \frac{\dot{u}^2}{uc^2} \cdot \frac{1}{1 - \beta^2} \cdot \frac{1}{(r^2 + R^2 + z^2 - 2rR \cos \theta_1)}$$

in the direction of the axis of Z.

This flow of energy is zero when the electron is stationary and has a maximum value when $\beta = 1$, attaining an infinite value as the motion of the electron equals that of light. This shows that the high speed electrons are the most efficient radiators of energy. This energy also varies inversely as the square of the distance, as in the case of all radiant energy.

We are now in a position to calculate the force acting on an element of volume due to the radiation emitted from that particle.

$$F = E + \frac{1}{c} [uH],$$

$$\begin{aligned} F_R &= E_R + \frac{1}{c} [H_\theta \cdot u_z - H_z \cdot u_\theta], \\ &= 0. \end{aligned}$$

$$F_z = E_z + \frac{1}{c} [H_r \cdot u_\theta - H_\theta \cdot u_r],$$

$$= \frac{1}{c} \left\{ \frac{e}{4\pi} \cdot \frac{-u \cdot \dot{u}}{uc} \cdot \frac{1}{\sqrt{1 - \beta^2}} \cdot \frac{1}{(r^2 + R^2 + z^2 - 2rR \cos \theta_1)^{1/2}} \right\} = 0.$$

$$F_{\theta} = E_{\theta} + \frac{1}{c} \{ H_z \cdot u_r - H_r \cdot u_z \}$$

$$= \frac{e}{4\pi} \cdot \frac{-\dot{u}}{c^2} \cdot \frac{1}{\sqrt{1-\beta^2}} \cdot \frac{1}{(r^2 + R^2 + z^2 - 2rR \cos \theta_1)^{1/2}} = 0,$$

where F represents the force acting on unit charge and U_{θ} is the tangential velocity.

The force acting on an element of volume $d\tau'$ at any point P is therefore

$$F_r = 0,$$

$$F_z = \frac{e}{4\pi} \cdot \frac{-\dot{u}}{c^2} \cdot \frac{1}{\sqrt{1-\beta^2}} \cdot \frac{\rho d\tau'}{(r^2 + R^2 + z^2 - 2rR \cos \theta_1)^{1/2}},$$

$$F_{\theta} = \frac{e}{4\pi} \cdot \frac{-\dot{u}}{c^2} \cdot \frac{1}{\sqrt{1-\beta^2}} \cdot \frac{\rho d\tau'}{(r^2 + R^2 + z^2 - 2rR \cos \theta_1)^{1/2}}.$$

If we suppose that an electron is composed of a perfectly conducting sphere surrounded by an electrically charged shell of uniform surface-density, then the $\frac{1}{c} \iint [E \cdot H]_r ds$ over the entire inner surface of the shell is equal to zero. Thus we see that no energy is radiated inwardly.

Suppose we take any spherical element of volume $d\tau$, then the energy radiated from it, if it is of uniform density, is $\frac{1}{c} \iint [E \cdot H]_r ds$ over any surface enclosing the element

$$= \frac{\epsilon^2}{8\pi} \cdot \frac{\dot{u}^2}{uc^2} \cdot \frac{1}{1-\beta^2},$$

where ϵ is the elementary charge on this volume element.

Thus we see that each element of the electronic shell radiates the same amount of energy.

We shall now make use of the idea of electromagnetic mass in dealing with radiation. If electromagnetic energy possesses mass, then there ought to be an equilibrium established between the mutual force of attraction and the radiation forces. Thus the energy will condense around the electron until this equilibrium value is attained, when it will be emitted in quanta. The force acting on the element of volume due to the radiated energy is per unit volume

$$= - \frac{\partial}{\partial t} [E \cdot H].$$

But the amount of energy radiated is

$$= c[E \cdot H];$$

\therefore the force acting on unit energy density

$$= \frac{1}{c} \frac{\partial}{\partial t} \{ \log [E \cdot H] \},$$

according to the third law.

In this calculation we have taken account of the condensation of the energy.

The force per unit of mass

$$\frac{c}{2} \frac{\partial}{\partial t} \{ \log [E \cdot H] \}.$$

Now

$$\frac{\partial}{\partial t} \iiint \frac{\rho r \gamma}{h} ds d\phi dr = c \frac{\partial}{\partial t} \log [E \cdot H].$$

But this mass is similar to that due to a charged particle, so that the force of attraction is not the ordinary Newtonian force of gravitation but rather the electrostatic force, therefore multiplying by $10^{40} \div 4 \cdot 1$

$$\text{we have} \quad 4\pi\gamma\rho a \, da = \frac{4 \cdot 1}{10^{40}} \cdot \frac{\partial}{\partial t} \log [E \cdot H] \cdot ac,$$

where ρ is the density and da the thickness of the shell.

$$\text{But} \quad M = 4\pi a^2 \rho \, da = \frac{2E}{c^2}$$

where E is the total energy condensed.

$$\therefore \quad E = \frac{c^3}{\gamma} \cdot \frac{4 \cdot 1}{10^{40}} \cdot \frac{\dot{u}}{u} \cdot \frac{a^2}{4} \text{ app.}$$

But if we examine the equation for the intensities, we see that the frequency $2\pi\nu = \omega$,

$$\text{so that} \quad E = \frac{c^3}{\gamma} \cdot \frac{4 \cdot 1}{10^{40}} \cdot \frac{2\pi a^2}{4} \cdot \nu.$$

$$\therefore \quad h = 6 \cdot 57 \times 10^{-27} \text{ app.,}$$

taking the radius of the electron $= 1 \cdot 5 \times 10^{-13}$ [Lorentz's value].

Now, if the electron is revolving around in a circular orbit, a suggestion of which we have just availed ourselves, then the radiation ought to experience a centrifugal force.

The equation of equilibrium will be

$$4\pi\rho a \, da \cdot \gamma \cdot \frac{10^{40}}{4 \cdot 1} = \frac{\omega^2}{2} r^2,$$

$$\text{or} \quad E = \frac{4 \cdot 1}{10^{40}} \cdot \frac{c^2}{\gamma} \cdot (\omega r^2) a \cdot \omega$$

$$= \frac{4 \cdot 1}{10^{40}} \cdot \frac{c^2}{\gamma} (\omega r^2) 2\pi a \cdot \nu.$$

But $\omega r^2 = \text{const.}$ according to the theory of central forces, since the radiation force acts along the axis of Z, whereas the plane of revolution is the XY plane.

$$\begin{aligned} \therefore h &= \frac{4 \cdot 1}{10^{40}} \cdot \frac{9 \times 10^{20}}{6 \cdot 6 \times 10^{-8}} \{8(\pi)^{3/2} \sqrt{r}\} a \\ &= 5 \cdot 92 \cdot 10^{-27} \text{ app.} \end{aligned}$$

Both of these values are very nearly coincident with the experimental values of h , for our knowledge of a is very limited.

There is also another remarkable coincidence in these values. They show that the momentum due to radiation is identical with that due to the centrifugal force; another example of the Principle of Equivalence.

It is hardly necessary to add that this equation $E = h\nu$ has been made the starting-point of the quantum theory of stationary states.

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August 20, 1921.

LXIII. *The Effective Capacity of a Pancake Coil.*

By G. BREIT*.

Purpose.

IT has been shown in a previous paper† that the effective capacity of a coil may be computed as

$$C_0 = \int_{x_1}^{x_2} \frac{M(x)}{L} \left\{ \int_{x_1}^x \frac{\alpha(x)}{L} dx \right\} dx, \quad . \quad . \quad . \quad (1)$$

where

x is an arbitrary parameter along the wire ;

L is the inductance of the coil ;

$M(x)dx$ is the mutual inductance of the section between x and $x+dx$ to the rest of the coil ;

$\left(\frac{di}{dt}\right)\alpha(x)dx$ is the charge on the element dx , i being the current through the coil terminal ;

x_1, x_2 are the values of x at the coil terminals, the value x_1 corresponding to the ungrounded terminal of the coil.

The conditions which were assumed in deriving this formula are :—

- (1) The constant C_0 exists.
- (2) The product of the frequency used into the conductivity is so high that the wire of the coil may be considered as a perfect conductor: *i.e.*, the electric intensity is practically perpendicular to the surface of the wire at any instant.
- (3) The dimensions of the coil are sufficiently small to make it legitimate to neglect the phase differences introduced into the retarded potentials by currents and charges in different portions of the coil.
- (4) The formula still applies if C_0 is not a constant in general, but is constant within a range beginning at very low frequencies.

It is the purpose of this paper to apply this formula to the case of a pancake coil.

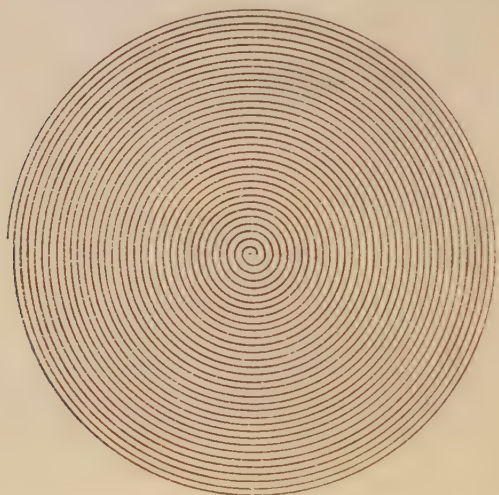
* Communicated by the Director of the Bureau of Standards, Washington.

† See "The Distributed Capacity of Inductance Coils," by G. Breit, Phys. Rev. xviii. p. 649 (1921).

Description of Pancake Coil.

By a pancake coil is meant a coil whose wires are all wound in one plane in a spiral, as shown on the figure (see fig. 1). It will be supposed that the number of turns

Fig. 1.--Pancake coil.



in the coil is large, that the turns are close together, and that the thickness of the insulation is negligible.

Thus the coil may be replaced by a disk on whose surface the potential varies in the same manner as it does in the coil.

Notation.

The radius of the pancake will be denoted by a .

Points in space will be referred to by cylindrical coordinates

$$(r, z, \theta),$$

with centre O at the centre of the coil, and with axis perpendicular to the plane of the coil.

Fig. 2.--Cross section of pancake coil by plane through diameter.



The meaning of these symbols is shown on fig. 2.

Simplifying Assumption as to Potential Distribution.

An arithmetical computation of the e.m.f. induced in various parts of the coil for a coil with a finite number of turns revealed the fact that the e.m.f. induced between a point on the surface of the coil and the centre is approximately proportional to the square of the distance of that point from the centre. The computation above mentioned consisted in calculating the e.m.f. induced between the centre and a number of points at various distances from the centre for the case of a coil having a finite number of equally spaced turns. Maxwell's formula in elliptic integrals was used, and numerical results were tabulated. These were then plotted, and the graph revealed the approximate relation stated.

The relation is frankly approximate, but is believed to be accurate enough for the calculation of the coil capacity. The computation which follows takes this for its starting-point.

General Plan of Attack.

The first step will be to compute the distribution of charge on the wires of the coil which will satisfy the law assumed for the potential distribution. Then the quantity $M(x)$ will be determined from the same law. The two expressions will next be substituted in (1), and hence C_0 will be obtained.

This will be done for three cases—namely that of the coil when ungrounded, and also when grounded—either at the centre or else at the outer edge.

The first part of the work consists, then, in the solution of an electrostatic problem—namely that of finding the charge distribution. The second part is ordinary integration.

Solution of the Electrostatic Problem.

It is convenient to transform the cylindrical co-ordinates

$$(r, z, \theta)$$

to elliptical co-ordinates

$$(u, v, \theta)$$

by the formula

$$r + jz = a \cosh(u + jv), \quad . \quad . \quad . \quad (2)$$

where

$$j = \sqrt{-1},$$

or its equivalents

$$\left. \begin{aligned} r &= a \cosh u \cos v, \\ z &= a \sinh u \sin v. \end{aligned} \right\} . \quad . \quad . \quad (3)$$

The surface $u = \text{constant}$ gives a spheroid of revolution whose equation is

$$\frac{r^2}{a^2 \cosh^2 u} + \frac{z^2}{a^2 \sinh^2 u} = 1, \quad . \quad . \quad . \quad (4)$$

as is seen by eliminating v from (3); and the surface $v = \text{constant}$ gives a hyperboloid of revolution whose equation is

$$\frac{r^2}{a^2 \cos^2 v} - \frac{z^2}{a^2 \sin^2 v} = 1, \quad . \quad . \quad . \quad (5)$$

as is seen by eliminating u from (3).

The two sets of surfaces represented by (4) and (5) are orthogonal because (2) is a conformal transformation. Also the planes $\theta = \text{constant}$ are perpendicular to both (4) and (5). Thus the co-ordinates (u, v, θ) are orthogonal.

It is readily shown that the Laplacian in these co-ordinates is

$$\begin{aligned} \frac{1}{\cosh u} \frac{\partial}{\partial u} \left(\cosh u \frac{\partial V}{\partial u} \right) + \frac{1}{\cos v} \frac{\partial}{\partial v} \left(\cos v \frac{\partial V}{\partial v} \right) \\ + \frac{\cosh^2 u - \cos^2 v}{\cosh^2 u \cos^2 v} \cdot \frac{\partial^2 V}{\partial \theta^2} = 0. \end{aligned}$$

In particular, if V is independent* of θ ,

$$\nabla^2 V = \frac{1}{\cosh u} \frac{\partial}{\partial u} \left(\cosh u \frac{\partial V}{\partial u} \right) + \frac{1}{\cos v} \frac{\partial}{\partial v} \left(\cos v \frac{\partial V}{\partial v} \right). \quad (6)$$

* This expression may be derived by remembering that if

$$x_1, \quad x_2, \quad x_3$$

are three orthogonal co-ordinates of such a kind that the differentials of length corresponding to the three differentials

$$dx_1, \quad dx_2, \quad dx_3$$

are

$$\frac{dx_1}{h_1}, \quad \frac{dx_2}{h_2}, \quad \frac{dx_3}{h_3};$$

then

$$\begin{aligned} \nabla^2 V = h_1 h_2 h_3 \left\{ h_1 \frac{\partial}{\partial x_1} \left(\frac{h_1}{h_1 h_3} \frac{\partial V}{\partial x_1} \right) + h_2 \frac{\partial}{\partial x_2} \left(\frac{h_2}{h_1 h_3} \frac{\partial V}{\partial x_2} \right) \right. \\ \left. + h_3 \frac{\partial}{\partial x_3} \left(\frac{h_3}{h_1 h_2} \frac{\partial V}{\partial x_3} \right) \right\}. \end{aligned}$$

See W. E. Byerly, 'Fourier Series and Spherical Harmonics,' p. 239, equation (6).

It is advantageous to transform this by

$$\left. \begin{aligned} \mu &= \sin v, \\ \nu &= j \sinh u, \end{aligned} \right\} \quad \dots \quad (7)$$

which reduces (6) to

$$\nabla^2 V = - \frac{\partial}{\partial \nu} \left\{ (1 - \nu^2) \frac{\partial V}{\partial \nu} \right\} + \frac{\partial}{\partial \mu} \left\{ (1 - \mu^2) \frac{\partial V}{\partial \mu} \right\} \dots \quad (8)$$

Now the electrostatic problem to be solved is that of finding for V a solution which together with its first derivatives is finite and continuous, which is independent of θ , which satisfies the Laplacian

$$\nabla^2 V = 0 \quad \dots \quad (9)$$

which vanishes at infinity at least to the first order and which at the disk becomes

$$V = V_0 - L \frac{r^2}{a^2} \frac{di}{dt} \quad \dots \quad (10)$$

But the equation of the disk is

$$u = 0;$$

in which case (3) reduces to

$$r = a \cos v.$$

Hence, using (7), equation (10) becomes

$$V = V_0 - L(1 - \mu^2) \frac{di}{dt} \quad \dots \quad (11)$$

Now the expression

$$[\alpha_n P_n(\nu) + \beta_n Q_n(\nu)] [a_n P_n(\mu) + b_n Q_n(\mu)],$$

where P_n , Q_n are Legendre functions of the first and second kind respectively, when substituted in (9) satisfies (9) in virtue of (8). If, then, one should be able to find such values of α_n , β_n , a_n , b_n , and such values of n that

$$V = \sum_n [\alpha_n P_n(\nu) + \beta_n Q_n(\nu)] [a_n P_n(\mu) + b_n Q_n(\mu)]$$

should vanish at infinity to the first order and should degenerate into (11) when ν approaches zero along the axis of pure imaginaries, then, in virtue of the uniqueness of the solution of (9) for given boundary conditions, the summation written gives the value of V .

If the summation written is an infinite series it also gives V , provided it is universally convergent as to μ and ν .

Further, for a given ν , V may be represented by a series of the form

$$\sum_{n=0}^{\infty} A_n P_n(\mu),$$

the summation being taken over all positive integral values of n , because V obviously satisfies the conditions which make such an expansion legitimate. The coefficient A_n is independent of μ but, for different values of ν , varies and is thus a function of ν . It must be clearly of the form

$$A_n = \alpha_n P_n(\nu) + \beta_n Q_n(\nu),$$

for otherwise (9) would not be satisfied. Here n is a positive integer. The function $P_n(\nu)$ is therefore a finite polynomial*, viz.

$$P_n(\nu) = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{1 \cdot 2 \cdot 3 \cdots n} \left[\nu^n - \frac{n(n-1)}{2(2n-1)} \nu^{n-2} + \frac{n(n-1)(n-2)(n-3)}{2 \cdot 4(2n-1)(2n-3)} \nu^{n-4} - \cdots \right],$$

and $Q_n(\nu)$ is an infinite series when $|\nu| > 1$, viz.

$$Q_n(\nu) = \frac{1 \cdot 2 \cdots n}{1 \cdot 3 \cdot 5 \cdots (2n+1)} \left\{ \frac{1}{\nu^{n+1}} + \frac{(n+1)(n+2)}{2(2n+3)} \frac{1}{\nu^{n+3}} + \frac{(n+1)(n+2)(n+3)(n+4)}{2 \cdot 4(2n+3)(2n+5)} \frac{1}{\nu^{n+5}} + \cdots - \cdots \right\}.$$

But points at infinite distance from the origin are given by real, positive, infinitely large values of u , and consequently in accordance with (7) by infinitely large values of ν on the positive half of the axis of pure imaginaries. Such values can be denoted as usual by $+j\infty$. It is clear that if $n > 0$, the expression for $P_n(\nu)$ becomes infinite for $\nu = +j\infty$ because it is a sum of terms of the same sign, and each term becomes infinite. Hence, if $n < 0$, $\alpha_n = 0$.

Further, there is symmetry about the plane $z = 0$. Hence by (3) and (7) only even values of n can be taken. Thus the most general possible expression for V is

$$V = \sum_{n=1}^{\infty} a_{2n} P_{2n}(\mu) Q_{2n}(\nu). \quad . \quad . \quad . \quad (12)$$

The coefficients A , a_{2n} must now be determined in such a way that

$$\sum_{n=0}^{\infty} a_{2n} P_{2n}(\mu) Q_{2n}(j \cdot 0) \equiv V_0 - L(1 - \mu^2) \frac{di}{dt}, \quad . \quad . \quad . \quad (13)$$

* See W. E. Byerly, 'Fourier Series and Spherical Harmonics,' p. 145, equations (9) and (10).

where the symbol $Q_{2n}(j, 0)$ stands for the limit of $Q_{2n}(j, \delta)$ as δ approaches zero taking only real and positive values.

Since now

$$1 - \mu^2 = \frac{2}{3} [P_0(\mu) - P_2(\mu)],$$

all a_{2n} but a_0, a_2 vanish, and a_0, a_2 are determined by the relations

$$\left. \begin{aligned} a_0 Q_0(j, 0) &= V_0 - \frac{2}{3} L \frac{di}{dt}, \\ a_2 Q_2(j, 0) &= \frac{2}{3} L \frac{di}{dt}. \end{aligned} \right\} \dots \dots (14)$$

Thus

$$V = \frac{V_0 - \frac{2}{3} L \frac{di}{dt}}{Q_0(j, 0)} Q_0(j, \sinh u) + \frac{\frac{2}{3} L \frac{di}{dt}}{Q_2(j, 0)} Q_2(j, \sinh u) P_2(\mu). \dots \dots (15)$$

The surface density of charge in coulombs is obtained as

$$\sigma = - \frac{10^{-11}}{8 \cdot 989} \frac{K}{4\pi} \frac{\partial V}{\partial n},$$

where K is the dielectric constant of the medium, and $\frac{\partial V}{\partial n}$ is the directional derivative of V with respect to the normal drawn away from the surface. The same may be written as

$$\left. \begin{aligned} \sigma &= - \frac{\kappa}{4\pi} \frac{\partial V}{\partial n}, \\ \text{where } \kappa &= \frac{10^{-11}}{8 \cdot 989} K. \end{aligned} \right\} \dots \dots (16)$$

Now at the disk the normal is parallel to OZ. Hence

$$\frac{\partial V}{\partial n} = \left(\frac{\partial V}{\partial z} \right)_{z=0} \text{ if } z > 0 \quad \text{and} \quad - \left(\frac{\partial V}{\partial z} \right)_{z=0} \text{ if } z < 0.$$

Hence by (3)

$$\frac{\partial V}{\partial n} = \frac{1}{a |\sin v|} \left(\frac{\partial V}{\partial u} \right)_{u=0},$$

and by (15), (16)

$$\sigma = - \frac{\kappa}{4\pi a |\mu|} \left\{ \left(V_0 - \frac{2}{3} L \frac{di}{dt} \right) \frac{j Q_0(j, 0)}{Q_0(j, 0)} + \frac{2}{3} L \frac{di}{dt} \frac{j Q_2'(j, 0)}{Q_2(j, 0)} P_2(\mu) \right\}.$$

But it may easily be shown that *

$$\text{and} \quad \frac{j Q_0'(j \cdot 0)}{Q_0(j \cdot 0)} = -\frac{2}{\pi}$$

$$\frac{j Q_2'(j \cdot 0)}{Q_2(j \cdot 0)} = -\frac{8}{\pi}.$$

Hence

$$\sigma = \frac{\kappa}{2\pi^2 a |\mu|} \left\{ \left(V_0 - \frac{2}{3} L \frac{di}{dt} \right) + \frac{8}{3} L \frac{di}{dt} P_2(\mu) \right\}. \quad (17)$$

This solves the electrostatic problem proposed.

Computation of the Function M(x).

In order to find the function $M(x)$, a choice must be made of the variable x . Here r will be chosen as this variable.

It was assumed that the e.m.f. varies as r^2 . This means that

$$\int_0^r M(r) dr = L \frac{r^2}{a^2};$$

or, differentiating,

$$M(r) = 2L \frac{r}{a^2}. \quad . \quad . \quad . \quad . \quad (18)$$

* These formulas can be derived from using the following facts:—

$$(a) \quad Q_0(z) = \frac{1}{2} \log \frac{z+1}{z-1}.$$

$$(b) \quad \frac{1}{y-z} = \sum (2n+1) P_n(z) Q_n(y).$$

(c) The recurrence formulas

$$(2n+1)zP_n(z) = (n+1)P_{n+1}(z) + nP_{n-1}(z).$$

Using (c) in (b), the expression for Q_{2m} in terms of Q_0 can be derived by writing the identity

$$\frac{y}{y-z} - \frac{z}{y-z} = 1.$$

Then from (a) expressions for Q_{2m} are obtained. On differentiating these expressions and passing the limit in the result of the differentiation as well as the original, the result follows at once.

Computation of the Function $\alpha(x)$.

As stated in the introduction, the differential of charge is

$$\frac{di}{dt} \alpha(x) \cdot dx.$$

The independent variable here chosen is r . As r varies from 0 to a , and as θ varies from 0 to 2π , the whole coil is traversed by the point (r, θ) . The differential of area is $2\pi r dr$, and the differential of charge is then $4\pi\sigma r dr$, where σ is given by (17) because expression (17) gives the surface density only on one side of the coil.

By (3), on the coil r becomes $a \cos v$; so that

$$\mu = \sqrt{1 - \cos^2 v} = \sqrt{1 - \frac{r^2}{a^2}}.$$

Substituting this in (3), and expressing the fact that

$$4\pi\sigma r dr = \left(\frac{di}{dt}\right) \alpha(r) dr,$$

it is found that

$$\alpha(r) = \frac{2\kappa r L}{\pi \sqrt{a^2 - r^2}} \left\{ \left(\left(\frac{di}{dt}\right) L - \frac{2}{3} \right) + \frac{8}{3} P_2 \left(\sqrt{1 - \frac{r^2}{a^2}} \right) \right\}. \quad (19)$$

It now remains to substitute (18), (19) into (1). If the ungrounded condenser terminal is connected to the centre, x_1 is to be taken as 0 and x_2 is to be taken as a . If, however, it is connected to the periphery, x_1 is to be taken as a and x_2 as 0.

The first of these gives

$$C_0 = \frac{4\kappa a}{\pi} \left[\frac{1}{15} + \frac{1}{6} L \frac{V_0}{\frac{di}{dt}} \right], \quad \quad (20)$$

and the second

$$C_0 = \frac{4\kappa a}{\pi} \left[\frac{2}{5} - \frac{1}{3} L \frac{V_0}{\frac{di}{dt}} \right]. \quad \quad (21)$$

If, now, the coil should be used with the centre grounded, and the ungrounded terminal of the condenser should be connected to the periphery, formula (21) applies, and in that formula $V_0 = 0$. This gives

$$C_0 = \frac{8\kappa a}{5\pi} \quad (22)$$

This is the effective capacity if the centre is grounded.

Again, if the periphery is grounded and the centre is not, formula (20) applies, and in that formula $V_0 = L \frac{di}{dt}$, as is seen from (10) by setting $V=0$ when $r=a$. This gives

$$C_0 = \frac{14\kappa a}{15\pi} \cdot \cdot \cdot \cdot \cdot \cdot \quad (23)$$

for the capacity with periphery grounded.

Finally, if the coil is insulated and the condenser is unshielded, as much current enters the coil as leaves it; so that (20) and (21) must give the same value for C_0 .

Multiplying (20) by 2 and adding to (21), it is found that

$$C_0 = \frac{32\kappa a}{45\pi} \cdot \cdot \cdot \cdot \cdot \cdot \quad (24)$$

if the coil is ungrounded.

It is worth mentioning that if C_0 be eliminated from (20) and (21), it is found that $\frac{V_0}{L} \frac{di}{dt} = \frac{2}{3}$, which, in virtue of the identity

$$\int_0^1 P_2(\mu) d\mu = 0,$$

shows in a different way that the coil is insulated.

Expressing the results in micromicrofarads, the capacity is

when grounded at centre.....	0.567 Ka $\mu\mu f$,
when grounded at periphery ...	0.330 Ka $\mu\mu f$,
when insulated	0.252 Ka $\mu\mu f$.

Now, according to the results of a previous calculation *, the effective capacity of a pancake coil of small depth when insulated is 0.437 Ka.

Thus, so far as the effective capacity is concerned, there is an advantage in using pancake coils of large depth as compared to pancake coils of small depth.

Experimental Verification.

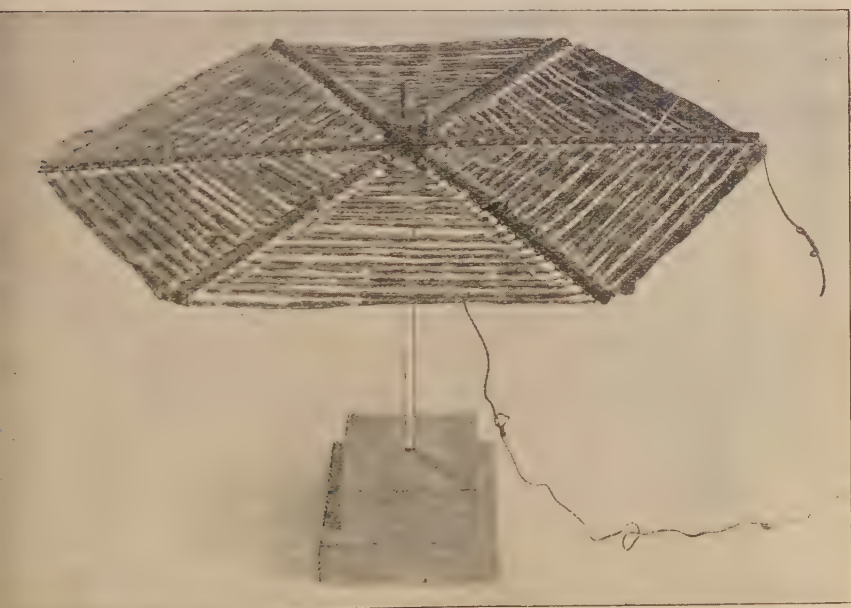
The formulas (22), (23) have been verified experimentally on a coil which is shown in fig. 3. This coil is not circular

* See G. Breit, *l. c.*

but hexagonal. The quantity a is therefore not quite certain.

In the computations it was taken as the mean of the radii of the inscribed and escribed circles, which are 26.5 cms. and 29.5 cms. respectively. Hence the mean is 28 cms. The dielectric being air, the capacity with centre grounded should be $16\ \mu\mu\text{f}$, and if grounded at the periphery it should be $9\ \mu\mu\text{f}$. The values as measured are $16\ \mu\mu\text{f}$ and $9\ \mu\mu\text{f}$.

Fig. 3.—Photograph of pancake coil.



Measurements were not made more accurately than $1\ \mu\mu\text{f}$, on account of the difficulties connected with such measurements.

The capacity of the same coil was also measured without the copper foil, leaving only the copper braid. No change was detected in the capacity.

It also appeared that the copper rods used in fastening the braid could affect the capacity. A row of them was soldered to the braid, but no detectable change in capacity was noticed.

The effective capacity of a pancake coil has been calculated, and the calculations have been verified experimentally in two cases.

The results of the calculation are that the capacity of the coil

when grounded at centre is $0\cdot567 Ka \mu\mu f$,

when grounded at periphery is ... $0\cdot330 Ka \mu\mu f$,

when insulated is $0\cdot252 Ka \mu\mu f$,

where a is the radius of the coil and K is the dielectric constant of the medium.

Washington, D.C.

Jan. 14, 1922.

LXIV. *The Relativity-Contraction in a Rotating Shaft moving with Uniform Speed along its Axis.* By FELIX E. HACKETT, M.A., Ph.D., Professor of Physics, College of Science for Ireland, Dublin *.

§ 1. Introduction and Summary.

A SOLUTION is offered in this paper of the problem of the relativity-contraction in a rotating shaft moving with uniform velocity along its own axis. The standpoint adopted is that of the fixed æther and the FitzGerald-Lorentz contraction combined with the restricted principle of relativity. The validity of Euclidean geometry is assumed throughout the paper.

A hypothetical modification of Fizeau's method for measuring the velocity of light is considered—a rotating shaft carrying two disks with apertures which correspond to the toothed wheel in Fizeau's experiment. It follows readily that when a rotating shaft is moving with uniform velocity along its own axis, to a stationary observer, looking in the direction of motion, it appears twisted in the opposite sense to the rotation. This effect has been pointed out by R. W. Wood †, and he has discussed the experiment, but not in a sufficiently precise way to serve as a basis for the subsequent discussion in this paper.

The arrangement may act as a clock. It measures time

* Communicated by the Author. Read at the meeting of the British Association, September 1921.

† Wood, 'Physical Optics,' 2nd edit. p. 690.

on the same principle as the ideal clock consisting of a beam of light reflected between two mirrors, with the addition that a disk fixed on the shaft at any cross-section and rotating with it can, owing to the twist, indicate the local time there.

In the latter part of the paper, the contraction in the shaft due to the motion of translation and the twist is considered as a strain-displacement. One of the principal axes of the strain is assumed to be the direction of resultant velocity $\sqrt{v^2 + u^2}$. The principal contraction in the latter direction is found to be $\sqrt{1 - (v^2 + u^2)/c^2}$.

This result holds for a shaft of any form, since the twist and longitudinal contraction do not depend on the form of the shaft. Passing from the case of a solid circular cylinder to the limiting case of a disk rotating without any motion of translation, the reasoning in this paper gives the circumferential contraction as equal to that usually accepted for a rotating ring, viz. $\sqrt{1 - u^2/c^2}$, where u is the velocity at the rim. It follows that the contraction in the radius is of the same magnitude.

§ 2. *The Velocity of Light and a Rotating Shaft.*

Stationary System.—A rotating shaft can serve in theory for the determination of the velocity of light by the following modification of Fizeau's experiment. Two similar disks are mounted on the shaft in planes normal to the axis separated by a distance l . Each disk is perforated by a number of equidistant apertures lying on a circle concentric with the shaft. In the subsequent discussion we ignore ordinary elastic strains, or, in other words, assume that the elastic constants are infinite.

The axis of the shaft is taken as the axis of z . The disks are similarly placed so that the apertures in each disk pass simultaneously through the plane of (x, z) as the shaft turns. We need only consider light rays travelling in this plane parallel to the axis of the shaft so that they can pass through an aperture in each disk for suitable speeds of rotation. Let the period of the lowest of these speeds be T . For this speed, light travelling through an aperture in one disk towards the other will pass through another aperture there which has just been brought into position by a rotation of the shaft through an angle ϕ , where ϕ = angle between two successive apertures in either disk. We have then

$$\phi \cdot c \cdot T/2\pi = l. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Moving System.—On the theory of restricted relativity, if the apparatus is transferred to a system S' moving with speed v along the axis of z and parallel to the axis of the shaft, the properties of the system remain unaltered. For the moving observer there are, therefore, definite speeds of rotation for which

- (1) light rays parallel to the axis of the shaft can pass through the apertures in the disks in either direction,
- (2) the measured speed of light in this hypothetical experiment is c .

To an observer in the stationary system, this is impossible unless compensations take place. He knows

- (3) the velocity of the moving system,
- (4) the distance between the two disks modified by motion to $l\sqrt{1-v^2/c^2}$.

Reasoning on these data, he concludes that the experiment can only succeed if the forward end of the shaft when in rotation is *twisted*, with respect to the rear end, *in the opposite sense* to the rotation through an angle, say θ ; and this twist must be such as to compensate for the different light-times between the disks in and opposite to the direction of motion. During the light-time for the former direction the shaft turns through an angle $\phi + \theta$, while the light has the relative velocity $c - v$. In the other direction, the shaft running at the same speed turns through an angle $\phi - \theta$, but the light has the relative velocity $c + v$. At this speed, condition (1) is satisfied, since light, emitted through an aperture in one disk towards the other, reaches it just as an aperture is passing across the path of the ray in the plane of (x, z) . The period of rotation T' and the twist required to satisfy this condition can be determined by the fixed observer using his own units from the equations:—

$$(c-v)(\phi + \theta)T'/2\pi = l\sqrt{1-v^2/c^2} = (c+v)(\phi - \theta)T'/2\pi,$$

which give

$$\theta/\phi = v/c,$$

$$\phi \cdot c \cdot (1-v^2/c^2)T'/2\pi = l\sqrt{1-v^2/c^2}.$$

Using (1) we get

$$T = T' \sqrt{1 - v^2/c^2}, \quad (2)$$

$$\theta = \frac{lv}{c^2 \sqrt{1 - v^2/c^2}} \cdot \frac{2\pi}{T'} = \frac{lv\omega}{c^2 \sqrt{1 - v^2/c^2}}. \quad . . . (3)$$

For the moving observer, however, there is no twist in the shaft. His units of time and length have altered, so that equation (1) holds giving the speed of light as c .

§ 3. Relativity Clocks.

This combination of rotating shaft and disks may be regarded as a set of relativity clocks regulated by the property that the shaft must rotate with the slowest speed ω for which it can transmit light through the apertures in either direction. The fixed observer considers that such clocks in the moving system run slow according to (2). It will be shown below that there is an automatic synchronization of the clocks. This is produced by the twist in the mechanical coupling, and satisfies Einstein's test for synchronism.

In the simplest form, each disk can serve as a local clock. To give the same value to c , the same method of fixing the unit of time must be adopted in all systems. It is convenient, here, to take as the unit the time of describing one radian. Using this unit, the angular position in radians of a special aperture with respect to (x, z) gives the time directly, and from (2)

$$\omega = \sqrt{1 - v^2/c^2} = \text{angular velocity of } S' \text{ shaft in } S\text{-units.} \quad (4)$$

To the moving observer there is no twist in the shaft. If he arranges that the timing aperture shall lie for every disk in the plane of (x, z) when the shaft is not rotating, he will conclude that in rotation the timing apertures pass through this plane "simultaneously".

It is easily seen that Einstein's test for synchronism is satisfied. The first disk may be taken as the origin, and the second at $x' = lS'$ -units since S' ignores the contraction. Let all the apertures be numbered in the opposite sense to the rotation 0, 1, 2, 3, etc., beginning from the timing aperture, and let mirrors be fitted into the apertures in the second disk. For the speed ω , a ray leaving the first disk by No. 0 aperture is reflected at the second disk by No. 1 mirror at x' and returns through No. 2 aperture. Thus the time of

arrival at $x' =$ mean of departure and arrival times at the origin.

According to the reckoning of the fixed observer, however, the passage of the timing aperture at x' through the plane of (x, z) is from (3) later than at the origin by $x'v\omega/c^2 \sqrt{1-v^2/c^2}$ owing to the twist in the shaft. This is the local time effect and leads to the Lorentz time-transformation adopting the usual conventions.

Counting time from the instant when the origins in each system coincide and the timing aperture at the origin in S' passes through the plane of (x, z) , we have at every point along the shaft

$$t \text{ in } S\text{-time} = \frac{\text{rotation of the } S' \text{ shaft}}{\text{its angular velocity in } S\text{-units}}$$

The rotation of the S' shaft is got by adding the twist to the angular distance of the timing aperture from the plane of (x, z) . The latter is t' in the units we have adopted, and from (3) and (4) we have $\theta = x'v/c^2$, giving

$$t \text{ in } S\text{-units} = \frac{1}{\sqrt{1-v^2/c^2}} (t' + \theta) = \frac{1}{\sqrt{1-v^2/c^2}} (t' + x'v/c^2). \quad (5)$$

§ 4. *The Strain in the Rotating Shaft.*

The discussion in § 2 has shown that to a fixed observer a rotating shaft with a motion of translation in the direction of its own axis is in a state of strain. For convenience the term contraction is used here for the ratio of new length to original length. We shall now proceed to find the principal contractions for this state of strain. For the sake of clearness, the assumptions involved in this discussion are set forth below.

We have as data the following *deductions* from the application of the principle of Restricted Relativity to the systems considered in § 2:—

(I.) The twist in the shaft is independent of its radius, whether it is hollow or solid, and is given by (3).

(II.) The FitzGerald-Lorentz contraction of the distance between two planes perpendicular to the axis is not altered by the rotation, otherwise the relations deduced in (2), (3), and (5) in agreement with the ordinary theory could not exist.

The contractions of the relativity theory are independent

of the physical characteristics of the body, and consequently, as already stated (§ 2), the fixed observer eliminates from his consideration any distortion due to centrifugal forces by the following condition:—

Ordinary elastic strains are ignored or, in other words, it is assumed that the elastic constants are infinite.

He interprets his observations in terms of Euclidean geometry, and so he makes the following geometrical assumptions:—

- (A) Each cross-section of the shaft remains a Euclidean plane, so that its radius alters in the same ratio as its circumference.

Assumption (A) is the only possible one from the Euclidean standpoint. Its justification lies in the simple form in which the principal contractions appear below.

Using these deductions and the foregoing assumption, it will be seen below that we can derive expressions for the contractions along the principal axes if we know their position. At this stage a further assumption must be made, more speculative than the preceding which arises directly from the Euclidean point of view of the fixed observer. According to (A) one of the principal axes of strain lies along the radius, *i. e.* along the direction of the centripetal acceleration. The other two must then lie in a plane normal to the radius, and we assume that

- (B) one of these lies along the direction of resultant velocity.

This last assumption may be justified by analogy with the Wiedemann effect. To a fixed observer a rotating shaft in the form of a thin tube moving along its own axis will be in a state of strain similar to that of a steel tube placed in a coaxial spiral magnetic field. In this instance, if hysteresis be eliminated, as it can be by special experimental methods, one of the principal contractions must be along the resultant magnetic field. The formula for the twist in the tube, deduced on this assumption, has been confirmed by experiment. In one case the tube is twisted by a spiral magnetic field, and in the other by its spiral motion. The physical analogy is so close that it seems to the author to justify the fixed observer in applying the same analysis to the twist in each case and in making assumption (B) about the direction of the principal axis.

We shall now examine the state of strain in the shaft from the point of view detailed above. In considering the analogy

of the Wiedemann effect the shaft was taken as a thin tube; this restriction is not necessary for the general mathematical treatment, as can be seen by reference to deduction (I.), though it may be helpful to think of the shaft as a thin tube in the following discussion.

We consider that the new co-ordinates x', y', z' of any point, as interpreted by the fixed observer, are given in terms of the original co-ordinates as in the ordinary strain theory. The axis of the shaft is taken as the axis of z . The fixed observer infers a rotation $\theta' = \tau z$ according to (3), and a FitzGerald-Lorentz contraction parallel to z according to deduction (II.). In accordance with assumption (A), each radius in any plane parallel to (x, y) is assumed to be contracted in a ratio which depends only on r , and the circumference alters in the same ratio.

As the rotation θ' cannot be assumed generally to be small, the steps of deducing the strain-components are given below:—

$$x' = ex \cos \theta' - ey \sin \theta',$$

$$y' = ex \sin \theta' + ey \cos \theta'.$$

We get for the relative displacement $\xi'_t, \eta'_t, \zeta'_t$ around x, y, z , of a point whose undisplaced co-ordinates are $x + \xi, y + \eta, z + \zeta$:

$$\xi'_t = \xi \frac{\partial x'}{\partial x} + \eta \frac{\partial x'}{\partial y} - \zeta \tau y',$$

$$\eta'_t = \xi \frac{\partial y'}{\partial x} + \eta \frac{\partial y'}{\partial y} + \zeta \tau x'.$$

But part of these relative displacements is a pure rotation θ' around an axis through x', y', z' parallel to the axis of the cylinder and arising from the general rotation. We shall obtain the strain components ξ', η', ζ' by combining the total effect $\xi'_t, \eta'_t, \zeta'_t$ with a rotation $-\theta'$, where

$$\xi' = \xi'_t \cos \theta' + \eta'_t \sin \theta',$$

$$\eta' = -\xi'_t \sin \theta' + \eta'_t \cos \theta'.$$

Whence

$$\xi' = \xi \frac{\partial(ex)}{\partial x} + \eta \frac{\partial(ex)}{\partial y} - \zeta \tau (ey),$$

$$\eta' = \xi \frac{\partial(ey)}{\partial x} + \eta \frac{\partial(ey)}{\partial y} + \xi \tau (ex).$$

When we refer to a point $x = r$, $y = 0$, we get

$$\xi' = \xi \left(e + r \frac{\partial e}{\partial r} \right) + \eta r \frac{\partial e}{\partial y}, \quad . \quad . \quad . \quad (6)$$

$$\eta' = e\eta + er\tau\zeta, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\zeta' = f\zeta. \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The radial strain at any point is determined by equation (6). To find the principal axes of strain in the plane of (y, z) we need only consider equations (7) and (8), which may be written

$$\eta' = e\eta + s\zeta, \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

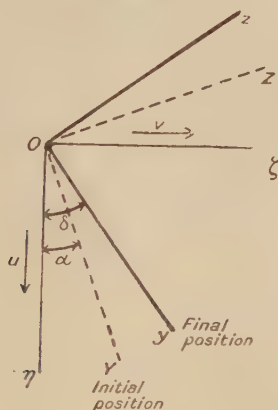
$$\zeta' = f\zeta, \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where $s = er\tau, \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$

$$f = \sqrt{1 - v^2/c^2} \quad \text{by deduction (II.).} \quad (12)$$

The next step is to express e, f, s in terms of the position of the principal axes and their contractions. Since the strain is not pure, the principal axes will be rotated from their initial positions, and both their final and initial positions will have to be considered.

Fig. 1.



We assume this part of the strain is produced by contractions along and perpendicular to axes Y and Z, which in consequence of the strain have been rotated into positions y and z , as shown in the diagram.

We have

$$y' = pY,$$

$$z' = qZ.$$

The co-ordinates y, z and axes Y, Z introduced here have no reference to the co-ordinates and axes used to deduce equations (6), (7), (8).

Returning to η, ξ axes, we have

$$\eta' = y' \cos \delta - z' \sin \delta,$$

$$\xi' = y' \sin \delta + z' \cos \delta,$$

$$Y = \eta \cos \alpha + \xi \sin \alpha,$$

$$Z = -\eta \sin \alpha + \xi \cos \alpha,$$

which give

$$\begin{aligned} \eta' &= \eta(p \cos \alpha \cos \delta + q \sin \alpha \sin \delta) \\ &\quad + \xi(p \sin \alpha \cos \delta - q \cos \alpha \sin \delta), \\ \xi' &= \eta(p \cos \alpha \sin \delta - q \sin \alpha \cos \delta) \\ &\quad + \xi(p \sin \alpha \sin \delta + q \cos \alpha \cos \delta). \end{aligned}$$

Comparing with (9) and (10), we get

$$e = p \cos \alpha \cos \delta + q \sin \alpha \sin \delta, \quad . \quad . \quad (13)$$

$$s = p \sin \alpha \cos \delta - q \cos \alpha \sin \delta, \quad . \quad . \quad (14)$$

$$f = p \sin \alpha \sin \delta + q \cos \alpha \cos \delta, \quad . \quad . \quad (15)$$

$$0 = p \cos \alpha \sin \delta - q \sin \alpha \cos \delta. \quad . \quad . \quad (16)$$

We get from (14), (15)

$$f \sin \delta + s \cos \delta = p \sin \alpha,$$

$$f \cos \delta - s \sin \delta = q \cos \alpha,$$

giving

$$p = (f + s \cot \delta) \frac{\sin \delta}{\sin \alpha}, \quad . \quad . \quad . \quad (17)$$

$$q = (f - s \tan \delta) \frac{\cos \delta}{\cos \alpha}; \quad . \quad . \quad . \quad (18)$$

from (16)

$$\frac{p}{q} = \frac{\tan \alpha}{\tan \delta}. \quad . \quad . \quad . \quad (19)$$

Thus

$$\frac{p^2}{q^2} = \frac{f + s \cot \delta}{f - s \tan \delta}, \quad \dots \quad (20)$$

$$e = q \frac{\sin \alpha}{\sin \delta}, \quad \dots \quad (21)$$

$$f = p \frac{\sin \delta}{\sin \alpha}. \quad \dots \quad (22)$$

At this point assumption (B) is introduced, *i. e.* one of the principal axes in the final position lies along the direction of resultant velocity, and we write

$$\tan \delta = v/u. \quad \dots \quad (23)$$

In the expression for the twist obtained in § 2 we have to note that θ' is in the opposite sense to ω , since translation is in the positive direction along z , and we introduce a negative sign, writing

$$\theta'/l = -\omega v/c^2 \sqrt{1 - v^2/c^2} = \tau;$$

hence

$$s = e r \tau = -u v / c^2 \sqrt{1 - v^2/c^2}, \quad \dots \quad (24)$$

and from (12)

$$f = \sqrt{1 - v^2/c^2}. \quad \dots \quad (25)$$

Inserting these values in (20), we find

$$p^2/q^2 = 1 - v^2/c^2 - u^2/c^2, \quad \dots \quad (26)$$

giving

$$\tan \alpha = v/u \cdot \sqrt{1 - v^2/c^2 - u^2/c^2}, \quad \dots \quad (27)$$

and from (23) and (27)

$$\sin \alpha = \sin \delta \sqrt{1 - v^2/c^2 - u^2/c^2} / \sqrt{1 - v^2/c^2}. \quad \dots \quad (28)$$

Inserting these values in (19), (21), and (22), we find the values of e , p , and q . The contractions are, most conveniently, stated for the surface of a cylindrical shaft having a uniform motion of translation v and a rotational speed u at the periphery, where both velocities are measured by the fixed observer.

Symbol.	Direction.	Contraction.
p	Resultant velocity.	$\sqrt{1 - v^2/c^2 - u^2/c^2}$.
e	Circumferential.	$\sqrt{1 - v^2/c^2 - u^2/c^2} / \sqrt{1 - v^2/c^2}$.
f	Longitudinal.	$\sqrt{1 - v^2/c^2}$.
q	Normal to acceleration and resultant velocity.	1.

The way in which the form for the simple longitudinal contraction is maintained in this more complex motion supports the assumptions which we have made, especially assumption (B), giving in (23) the direction of one of the principal contractions.

These results hold generally for any solid shaft in the same state of motion, since, as stated in deductions (I.) and (II.), § 4, the twist and longitudinal contraction are independent of the form of the shaft.

§ 5.* *The Contraction in a Rotating Disk.*

The expressions deduced in the last section hold for all values of v and u . They should hold in the limiting case for which $v=0$ when the shaft is rotating around an axis fixed relative to the observer. In this way we derive a solution of the problem of the rotating disk which enters so frequently into discussions of the restricted and general principles of relativity. Writing $v=0$, we find

$$\text{circumferential contraction} = \sqrt{1-u^2/c^2}.$$

Before discussing this result, it may be well to state the solutions which have been previously given of this problem. Following Ehrenfest, it has been frequently stated * that if a measuring rod is applied tangentially to the edge of a disk in rotation in its own plane about its centre, the rod is shortened in the direction of motion, but will not experience a shortening if it is applied to the disk in the direction of the radius. The result was originally put forward as a speculative inference from the restricted principle of relativity. It raised the difficulty that the ratio of the circumference to the diameter is no longer constant, but this has since been met by the statement that the disk is no longer a Euclidean plane.

On the other hand, Lorentz finds that both radius and circumference contract in the ratio of 1 to $1-v^2/8c^2$ from an investigation based on the general principle of relativity.

This problem is a special case of the "general question as to how far the dimensions of a solid body will be changed when its parts have unequal velocities, when, for example, it has a rotation about a fixed axis. It is clear that in such a case the different parts of the body will by their interaction hinder each other in the tendency to contract to the amount determined by $\sqrt{1-v^2/c^2}$ "†.

* Einstein, 'Theory of Relativity,' p. 81; Jeans, Proc. Roy. Soc. vol. 97. A, p. 68 (1920).

† Lorentz, 'Nature,' February 17th, 1921, p. 79.

The statement just made does not seem to apply to the problem treated in this paper. For the contraction due to the helical motion of the shaft is given in terms of the resultant velocity by the usual formula; and according to deduction (L.) in § 4 the state of strain in the periphery of a solid shaft is in no way different from that of a thin tube of the same external radius and in the same state of motion. In the limiting case no distinction can, therefore, be drawn between the strain in the rim of a rotating disk and a rotating ring. The radius of each must contract in the same ratio as the circumference, viz. in the ratio 1 to $\sqrt{1-u^2/c^2}$.

We have then $r_\omega = r \sqrt{1-\omega^2 r_\omega^2/c^2}$, where r_ω = radius when the angular velocity is ω ; this gives

$$dr = dr_\omega / (1 - \omega^2 r_\omega^2 / c^2)^{3/2}.$$

Summarizing these results, we have then:—

The radius and the circumference of a solid disk rotating with constant speed about an axis at right angles to its plane contract in the ratio of 1 to $\sqrt{1-u^2/c^2}$, where u is the velocity at the rim.

A measuring rod laid along the radius contracts in the ratio of 1 to $(1-u_1^2/c^2)^{3/2}$, where u_1 is the velocity at that position in the disk.

The simplicity of the assumptions made and the analysis given in this paper give support to the view that the above conclusion is correct, within the limitations of the Euclidean outlook adopted. It takes a middle course between the results stated by Einstein and Jeans and the solution given by Lorentz. It is conceivable that a solution may, however, be found beyond the limits of Euclidean geometry which may include all points of view.

§ 6. *Note on the Wiedemann Effect.*

A vertical iron wire carrying a current twists in a vertical magnetic field. This is recognized as an effect of magnetostriction due to the resultant magnetic field in the wire. The effect is simplified if a steel tube is used in which a spiral, or more accurately a helical, magnetic field acts whose axis coincides with the axis of the tube. This is produced by combining a longitudinal field with a circular field due to a current flowing in a wire passing along the axis of the tube.

The analysis given above immediately applies; we get from (11), (13), (14), and (19)

$$\theta'/l = \tau = s/er = \sin 2\delta/r \cdot p^2 - q^2/2pq.$$

In the case of magneto-striction we can write $p = 1 + \epsilon_1$ and $q = 1 + \epsilon_2$, where ϵ_1 and ϵ_2 are small. The difference between the position of the principal axis before and after the strain can be neglected so that $\delta = \alpha$, and we get

$$\theta' = \sin 2\alpha (\epsilon_1 - \epsilon_2) l/r.$$

This is the formula given by Knott and verified experimentally by the author*.

The author desires to express his obligation to Prof. W. McF. Orr, F.R.S., for his interest in and criticism of this paper.

LXV. *Breath Figures*. By T. J. BAKER, D.Sc. (Lond.)†.

IF one breathes upon a sheet of glass which has been cleaned with soap and water and polished with clean linen, water-vapour condenses uniformly on the glass in such a manner that the surface as seen by reflected light appears dull and rather white. If the tip of a small blowpipe-flame is caused to traverse the surface of such a plate and the plate is then breathed upon as soon as it is cold, a whitish condensation appears on those parts which the flame has not touched, whilst the track of the flame is marked by a form of condensation which, owing to its transparency, appears black by contrast with the neighbouring parts.

This and certain allied phenomena were described by Aitken‡ in 1893, and several letters discussing the subject appeared in the pages of 'Nature'§ during the period 1911 to 1913, but no general agreement as to the cause was reached.

A lens shows that the white portion of the deposit consists of lens-shaped drops which are isolated from each other, whilst the black condensation consists of a continuous film of water.

* Knott, Trans. Roy. Soc. Edin. vol. xxxv. p. 388; Hackett, Proc. Roy. Dub. Soc. vol. xv. (n. s.) p. 416.

† Communicated by the Author.

‡ Aitken, Proc. Roy. Soc. Edin. p. 94, 1893.

§ 'Nature,' May 25, June 15, July 6, 1911, Dec. 19, 1912, Feb. 6, 1913. See also vol. vii. of Lord Rayleigh's 'Collected Scientific Papers.'

The late Lord Rayleigh held the view that the part of the glass swept by the flame had been rendered cleaner than the neighbouring portion, whilst Aitken urged that the track of the flame had been rendered dusty by solid particles deposited from the flame, and that these particles aided condensation of moisture. He pointed out that by scraping with a match-stalk across the flame track a dusty deposit could be rubbed up, and he considered that this contamination of the surface is responsible for the breath figure. It is true that the track which an ordinary blowpipe-flame has followed can be detected by the eye before any moisture has been deposited on the plate, but a flame of carbon monoxide leaves no such deposit, and Aitken's explanation seems inadequate because this flame yields an excellent breath figure. Lord Rayleigh showed that if the outside of a test-tube were heated to redness the "black" or transparent condensation could be obtained on the corresponding part of the interior of the tube. This was at first contested by Aitken, who maintained that the flame, or the hot gases from it, must strike the glass directly to produce the result; but further experiments led him to accept Lord Rayleigh's statement, and he then suggested that a chemical change in the glass itself might account for the effect.

Quinke found that when a drop of strong sulphuric acid is warmed on a glass plate, which is afterwards washed and dried, the "black" condensation may be obtained on the part which has been exposed to the acid. Craig suggested that this might be due to the soaking in of the acid, thus forming a hygroscopic film; and as coal-gas always contains sulphur compounds, he contended that a coal-gas flame playing on glass might deposit enough sulphuric acid to act in this way. But it was known that a flame of pure hydrogen burning in air also gives breath figures, and Craig therefore suggested the possibility that some nitric acid might be formed by the flame, and that this acid might determine the production of a breath figure. If this is true, it follows that hydrogen burning in pure oxygen should fail to be effective. This summary fairly represents the main features of our knowledge of the subject up to 1913. From that date onwards the author has intermittently carried on the inquiry, with the result that other relevant phenomena have been discovered, and a partial explanation of the results can be offered.

Experimental.

With the exception of certain cases specifically mentioned, the surfaces used were first washed with soap and water, then rinsed with tap-water, dried with a clean cloth, and finally rubbed vigorously with a clean linen handkerchief until the white condensation produced by breathing lightly upon them showed uniformity. The surfaces so prepared will be described for convenience as "cleaned" surfaces. It must also be understood that the term "breath figure" connotes that condition of a surface which reveals itself by the black form of condensation. A breath figure is not visible until moisture condenses on the surface.

At the outset it seemed probable that a complex substance like glass was not best suited for the purpose, and some preliminary experiments were made with other materials. In general, it was found that the chemical composition of the substance is not important, because breath figures were easily obtained on porcelain, rock-crystal, mica, Iceland spar, platinum, nickel, silver, brass, and mercury. Aitken's suggestion that chemical change might explain the effect cannot be maintained in face of the fact that the figures can be obtained on rock-crystal and platinum. Again, since the burning of coal-gas in a blowpipe-flame might lead to the deposition on a cold surface of such substances as carbon, sulphur compounds, and tarry matter, it was decided to try the flames of hydrogen and carbon monoxide. Hydrogen prepared from hydrochloric acid and magnesium was passed through soda-lime to arrest any acid spray, and was burnt at a platinum jet. This flame produced excellent breath figures. Burning carbon monoxide from sodium formate and sulphuric acid gave equally good figures. From these experiments we may conclude that breath figures do not require for their production the deposition of any solid matter from the flame. Further, since no water is produced when carbon monoxide is burnt, the effect cannot be attributed to deposition of moisture.

Lord Rayleigh has pointed out that the pattern of a breath figure may be recorded permanently by the chemical deposition of silver on the glass plate. The track of the flame is distinctly marked by a difference in the appearance of the deposit, and this difference is most marked near the margins of the track, *i. e.* where the hottest part of the flame impinges on the glass. This was confirmed both when the flames of hydrogen and coal-gas were employed.

Influence of the temperature of the flame.

Aitken mentions that the flame of burning alcohol does not produce satisfactory breath figures. The author made a small spirit-lamp with a test-tube as reservoir and a tuft of glass-wool supported in a glass tube as wick. This was supplied with "industrial spirit," and was regulated to give a flame about $\frac{1}{4}$ inch high. No breath figures could be obtained, probably because such a small flame is not very hot. It was found that the larger flame of an ordinary spirit-lamp gave a breath figure, but the effect was distinctly weak.

Some methylated ether was purified by standing over caustic potash and potassium permanganate for several days and then distilling. The portion coming over at $34^{\circ}5$ was collected and used in the lamp described above. No breath figures were obtained. It may be noted that an ether flame always leaves a small deposit of soot on the plate, and the non-production of a breath figure in these circumstances seems to negative Aitken's suggestion that dust is an important factor.

If a mouth-blowpipe is used in conjunction with an alcohol or with an ether flame good figures are easily obtained.

Again, if a glass plate is drawn rapidly across the extreme tip of a well-shaped blowpipe-flame, the breath figure shows a perfectly uniform "black" track; but if the plate cuts across the flame near to the reducing cone, then the breath figure shows two clear "black" lines which correspond with the hot exterior of the flame, whilst the space between them exhibits more or less of the white condensation corresponding to the relatively cool interior of the flame.

These facts seem to indicate that the condition of the surface necessary for the production of these figures is only attained after it has been exposed to a flame whose temperature is above a certain minimum.

Sir J. J. Thomson ('Conduction of Electricity through Gases,' p. 194) says "ionized gas is produced by flames of coal-gas whether luminous or not, by the oxy-hydrogen flame, by the alcohol flame of a spirit-lamp, by a flame of carbonic oxide: it is not, however, produced in very low temperature flames such as the pale lambent flame of ether."

The parallelism between the ionizing effects of the flames mentioned in the foregoing abstract and the facts just stated in connexion with the production of breath figures suggests

the possibility that ions derived from the flame may be the cause of these figures; but the extraordinary permanence of the effects and the fact that actual contact with the flame gases is not essential render the hypothesis untenable.

Permanence of breath figures.

The peculiar condition of the surface of glass which causes it to reveal the flame-track when it is breathed upon is singularly permanent, and persists for many months. As stated by Lord Rayleigh and Mr. Aitken, a breath figure may be removed by rubbing with soap and water, but the author has occasionally experienced great difficulty in getting rid of the last traces of the effect. Rubbing with a dry cloth weakens the figures, but does not destroy them.

Experiments with chemically cleaned glass.

Up to this point the glass plates had been cleaned as described on page 754, and it now appeared necessary to examine the behaviour of glass which had been subjected to chemical cleansing processes such as are employed preparatory to silvering. After the final washing in distilled water the plates were supported on glass rods in a desiccator, and were left there until dry.

When these chemically clean plates were breathed upon the condensation was almost entirely of the "black" kind—or, in other words, the glass was covered with a continuous film of water. When a flame was made to traverse a chemically clean plate and was afterwards breathed upon, no breath figure, or at most a very imperfect one, appeared, thus suggesting that a film of some contaminating material must be present upon the glass before it is exposed to the action of the flame.

Glass plates which have been cleaned as described on page 754 are certainly covered with a contaminating film, and in this connexion the work of W. B. Hardy and J. K. Hardy (Phil. Mag. July 1919) is significant. These investigators found that truly clean glass surfaces will not slide over each other, but seize owing to cohesion. A very small amount of contamination lowers the resistance to relative motion, and sliding becomes possible. The author has applied this method to test the condition of the surfaces of glass plates used in obtaining breath figures, and the following details are representative of the results obtained.

A chemically clean watch-glass was placed on an equally clean sheet of plate glass as in Hardy's experiments, and it was found that a horizontal pull of 8 grams was needed to

start motion. This was not true sliding, but consisted of jerky movements accompanied by a gritty sound resembling that produced by a diamond when drawn across glass. One half of the glass surface was then rubbed with clean linen and the watch-glass was placed upon it, and it was found that a pull of 4 grams was sufficient to cause steady sliding without noise. Evidently the linen had contaminated the glass.

A blowpipe-flame (coal-gas) was now swept across that half of the sheet which had been rubbed with linen, and once across the unrubbed and therefore chemically clean half. Each of these flame tracks was tested with the watch-glass, and a pull of 5.5 grams was required in each instance to cause movement, and this motion was not smooth.

It appears reasonable to suppose that in one case the flame had removed the film of contamination left by the linen, and that in the other it had slightly contaminated the half which was chemically clean.

In another experiment the flame of pure carbon monoxide was used instead of a coal-gas flame, in order to eliminate the possibility of contaminating the glass by the products of combustion of coal-gas. Steady sliding of the watch-glass occurred on the linen-rubbed part with a pull of 4 grams; but when the watch-glass was placed on the track of the CO flame a pull of rather more than 7 grams was required, and the movement was of the type associated with a clean surface. This pull of 7 grams is very close to the value (8 grams) required on chemically clean glass. If a thin clean glass rod with a rounded end is drawn gently across a glass sheet which has been rubbed with clean linen it slides freely and noiselessly, but when it encounters a flame track the increased friction is easily felt, and a faint squeak may be heard.

Chemical deposition of silver on a flame track.

If a film of silver is deposited chemically on a sheet of "cleaned" glass across which a flame of carbon monoxide has been swept, it is seen that the mirror is whiter and freer from pin-holes on the flamed part than it is elsewhere. This points to the greater cleanliness of the flamed portion.

A test-tube was washed out with soapy water followed by tap-water, and was then thoroughly dried by rubbing the inside with clean linen. A narrow belt of the tube near its middle was then heated externally in a small Bunsen flame to a temperature which was much below its softening-point.

When the tube was cold a silvering solution was introduced, and the quality of the mirror obtained was better on the zone which had been heated than elsewhere. The borders of this belt were badly silvered, and it seems probable that the contaminating film which covered the interior of the tube had been driven from the heated belt to the cooler parts on each side of it, where the increased contamination would affect the deposition of silver adversely.

If the tube has been heated until softening is imminent, the silver deposits on this part in a manner which suggests that the original smoothness of the glass surface has been partially destroyed.

The point which was at issue between Lord Rayleigh and Aitken appears therefore to be decided in favour of the former, who believed that *the passage of a flame across the glass cleanses it*, and thus favours the condensation of moisture in the form of a continuous film instead of droplets.

Nitric acid not a cause of breath figures.

It remains to consider the suggestion of Craig, viz. that some nitric acid might be formed in a flame and be deposited on the glass, thus determining the formation of a breath figure. If hydrogen were burnt in pure oxygen this possibility would be excluded. A jet of hydrogen was ignited electrically in a large tube through which a stream of oxygen was passing, and by a simple device a small glass sheet was passed through the flame. The glass showed an excellent breath figure when breathed upon. The oxygen used was prepared in one case from sodium peroxide and water, and in another experiment from potassium permanganate, but absorption with pyrogallol showed that it contained rather more than 1 per cent. of (presumably) nitrogen. The result is not conclusive, because a small amount of nitric acid might have been formed; but it seems unlikely that the reduction of the nitrogen from 79 per cent. (in air) to about 1 per cent. should have been without influence on the strength of the breath figure if nitric acid plays any part in the process; and it is difficult to see how the presence of a minute quantity of acid could account for the great increase in friction described in the preceding section.

Transference of breath figures to a second plate.

In that which follows it will be convenient to refer to a plate which has been traversed by a flame as a "flamed" plate.

A flamed plate which had been used for certain experiments was by chance placed with its flamed surface downwards on another glass plate which had not been used. Next day the plates were separated, and it was observed that both plates gave breath figures, one being an exact copy of the other. Moreover, the original showed no diminution of intensity. This accidental observation was many times confirmed, and it became clear that closer investigation was necessary.

The transference of the effect from one plate to another lying upon it suggested that some volatile material was concerned in the process, and that the escape of this material might be assisted by reduction of pressure or by increase of temperature. A flamed glass was therefore put face to face with a "cleaned" sheet of glass and the two plates, clipped together, were placed in the receiver of an air-pump, and the pressure was reduced to a few cms. of mercury. A few minutes later the plates were withdrawn, separated, and breathed upon, when a perfect copy of the original was obtained on the "cleaned" plate, whilst the flamed plate still retained its power of producing a breath figure with unimpaired intensity.

Thus transference occurs as effectively in a few minutes under reduced pressure as it would in the course of hours under atmospheric pressure.

Experiments were then made with plates separated about $\frac{1}{2}$ mm., and a clear transfer was obtained in about 15 minutes. The separation was increased to about 2 mm., and again a transfer occurred, but much diminished in intensity. With a separation of 1 cm. it was not possible to detect with any certainty that transfer had occurred.

The flames of hydrogen and carbon monoxide also produced transferable figures; and, since neither of these gases yields solid products on burning, it appears unlikely that the volatile material causing the transfer can have been provided by the flame. It was also found that the transferred figure resembles the original in offering marked resistance to the steady sliding of a watch-glass across the glass plate, although the effect, as might be expected, is weaker. Whatever may be the explanation of the phenomenon of transfer, this fact indicates that *the transferred figure represents a portion of the glass which has been partially cleared of the contaminating film.*

At this point it was thought desirable to discover whether the peculiar properties of a flamed plate are modified by breathing upon it. One half of a flame track was covered up

and the other half was breathed upon. As soon as the deposited moisture had evaporated the protecting cover was removed, and the usual procedure for obtaining a transfer *in vacuo* was followed. Not the slightest difference in the two halves of the transfer could be detected. It is therefore permissible, and sometimes convenient, to test the flamed plate by breathing upon it before using it to obtain a transfer.

Length of time during which a flamed plate retains its power of giving a transfer.

A flamed plate was kept in a warm room for 60 hours, and at the end of this time it was left *in vacuo* for 24 hours in contact with a "cleaned" plate, and on this a good transfer was obtained. Another flamed plate after 9 days' exposure to the air behaved similarly, but the transfer was fainter; and in a third instance a plate produced a transfer 18 days after it had been flamed. The loss of the volatile material is plainly very slow under ordinary conditions of temperature and pressure.

Condition of the flamed plate after it has been exposed to reduced pressure.

A flamed plate was left *in vacuo* for 24 hours. It was then removed and clipped face to face with a "cleaned" plate, and the two were kept *in vacuo* for 20 hours. No transfer occurred, but the original flamed plate gave a breath figure as good as though it had not been exposed to low pressure. In a second trial the time allowed for transfer *in vacuo* was extended to 48 hours, but no trace of transference could be detected.

These facts seem to confirm the hypothesis that transference is due to the escape of material from the flamed track on the plate, and that the whole of this escapes under reduced pressure in the course of a day. At the same time it is clear that the surface of the glass which has lost this matter is still in an abnormal condition, and whatever this condition may be it is one which persists for many weeks.

Secondary transfer.

A transfer was obtained in the usual manner. The plate A on which this transfer had been effected was then clipped in contact with a "cleaned" plate B, and both were placed *in vacuo* for 10 minutes. At the end of this period they were separated, and plate B was examined. No transfer

could be detected. The plates were again put in contact and left *in vacuo* for 2 days, and then it was found that a transfer from A to B had occurred. Plate A still retained its power of producing a breath figure.

These secondary transfers afford further confirmation of the view that the substance which modifies the glass surface is volatile, and it is worthy of notice that the glass on which the first transfer was obtained still retained its property of yielding a breath figure.

Permanent record of a transferred figure.

When silver is deposited chemically on a glass sheet which has received a transfer, the pattern is recorded precisely in the same manner as the figure on the original flamed plate.

Transfer produced by heating the flamed plate.

A flamed plate and a "cleaned" plate were held face to face by clips, and the back of the flamed plate was heated by a Bunsen flame until it was uncomfortably hot to the touch. When cold the "cleaned" plate showed an excellent transfer, and the flamed plate itself still gave a perfect breath figure. The original flamed plate was now placed in contact with another "cleaned" plate, and the process was repeated. This resulted in a very clear transfer, but rather fainter than the first, indicating that not all the volatile matter had been expelled by the first heating.

Experiments were then made with the plates slightly separated, and transfers were obtained even when the distance between them was fully 2 mm., but the outlines of the figures were less distinct, probably owing to diffusion of the volatile matter during its passage across the intervening space.

Temperature required to expel the volatile matter.

The volatile matter is rapidly dissipated at 100° C., for it was found impossible to obtain a transfer from a flamed plate which had been heated in a steam-oven for $\frac{3}{4}$ hour. In this connexion Lord Rayleigh's observation that a breath figure may be obtained on the inside of a test-tube by heating it externally to redness may be recalled. Such a figure should be incapable of transference because the high temperature of the walls of the tube would have expelled any volatile matter which may have been there. To test the point a flat sheet of fused silica was held so that the tip of a small blowpipe-flame impinged on the middle of one face until a

red-hot spot was visible. When quite cold the face of the plate remote from the flamed face was placed in contact with a "cleaned" sheet of glass, and both were subjected to reduced pressure. No transfer was visible even after the lapse of 46 hours. A similar negative result is obtained if the flamed face of the silica plate is used.

Electric breath figures.

The tracks of electric sparks which have traversed the surface of a "cleaned" plate of glass are rendered visible by "black" condensation when the plate is breathed upon. Figures so obtained are transferable, and in all their properties resemble those produced by flames.

Electric discharges in air produce ozone, but the present Lord Rayleigh has shown that this gas does not yield breath figures on glass.

Nitric acid is also formed, but the author has found that good figures can be obtained on glass which has been traversed by sparks in an atmosphere of hydrogen. It is therefore unlikely that the figures are caused either by ozone or nitric acid. By passing a large number of sparks between two platinum sheets which rested upon a sheet of "cleaned" glass a well-defined area was obtained, which could be tested for friction by Hardy's method. To cause steady motion on the unsparked portion of the glass a pull of $4\frac{1}{4}$ grams on the watch-glass was sufficient, whilst on the sparked area a force of $7\frac{1}{2}$ to 8 grams weight was necessary to start motion. These results are almost identical with those obtained on the track left by the flame of carbon monoxide (p. 757), and it is highly probable that sparks remove the contaminating film from the glass surface either by their heating or disruptive effects.

It is well known that when a sheet of cleaned glass is placed upon an insulated metal plate which is connected to one pole of an induction-coil, and a coin, connected to the other pole, is laid on the glass, the passage of a discharge for a few seconds will produce the conditions for the development of a breath figure on the glass. The "black" condensation corresponds to those parts of the coin which are in relief and, in addition, the tracks of any sparks which may have traversed the glass surface from the edge of the coin will also be rendered evident as wavy lines of "black" condensation.

It may be assumed that discharges from the under surface of the coin to the glass beneath it occur most abundantly from those parts which are in highest relief, so that the film

of contamination is removed from those parts of the glass more rapidly than from the neighbouring areas, and a breath figure revealing the design of the coin may be developed. If the time during which the discharge takes place is too prolonged, the whole of the film beneath the coin is removed, all details disappear, and only a disk of "black" condensation is obtained when the glass is breathed upon.

Electrical conductivity of breath figures.

The author has found that the passage of a flame or of a stream of electric sparks across the surface of "cleaned" glass greatly reduces the insulating property.

Two ebonite rods were capped with small pads of tin-foil, one of which was earthed, and the other was connected by a wire to a charged electroscope. By pressing the two pads simultaneously on the surface of the glass to be examined any leakage across the intervening portion of the glass is easily detected.

Flame tracks produced by burning coal-gas, hydrogen, and carbon monoxide all show considerable conductivity. Coal-gas appears to be most effective, and this is not unlikely, because sulphurous acid is one of the products of its combustion.

If a flamed plate is heated in a steam oven for about 30 minutes the conductivity of the flame track is found to have been reduced very greatly, and a similar result is obtained after a flamed plate has been left *in vacuo* for a few hours. Transfers are also found to possess a certain small conductivity.

It is a matter of indifference whether the electroscope has been charged positively or negatively.

The reduction in conductivity brought about by heating to 100° , or by exposure to reduced pressure, suggests that water derived from the burning of the coal-gas or hydrogen may account for the effect, but it is not clear why the flame of carbon monoxide or electric sparks should produce conductivity.

Discussion of results.

It is probable that a breath figure produced by a flame or by electric sparks is to be attributed in part to the burning off or volatilization of the thin film of contamination which is present on a surface which has been rubbed with "clean" linen. The track of the flame or spark then presents an

uncontaminated surface on which moisture condenses in the form of a continuous transparent film.

It would be expected that the flame-cleaned track would speedily become contaminated again and cease to function, but the extraordinary persistence of the property associated with the production of a breath figure (p. 756) indicates that other factors have to be considered. What these factors are cannot be asserted with confidence, but it is not improbable that the structure of the surface layer of the glass itself suffers a change during its momentary exposure to a high temperature, and it is also possible that some of the decomposition products of the contaminating film are occluded by the glass along the flame track.

If a *chemically cleaned* sheet of glass is traversed by a flame of carbon monoxide, and, when quite cold, is immersed in a silvering solution, it is found that the silver begins to deposit first along the flame track. Since no film of contamination previously existed on the glass, it would appear that the difference in the rate of deposition of silver is due to a physical change in the surface of the glass.

It is more difficult to offer an explanation of the transference of a breath figure from a flamed plate to a "cleaned" plate, but since the process is hastened by reduction of pressure and by rise in temperature, and occurs even when the plates are not in contact, it is clear that some gaseous material passes from one to the other. Also, it has to be borne in mind that the transferred figure is an area from which the contaminating film has been more or less removed (p. 759).

We may imagine that the contaminating film on a "cleaned" plate tends to prevent the ready escape of gas-molecules which have been occluded by the glass surface, but that where this impediment has been removed by the passage of a flame, or by sparks, a violent outrush occurs when the temperature is raised or the pressure is reduced, and these molecules on striking the opposed surface of the "cleaned" plate break up and scatter that portion of the contaminating film on which they impinge and thus expose a relatively clean surface on which moisture will condense in the "black" form. This suggestion may be extended to explain a second transfer from the first.

The molecules which are active in producing this result probably arise from the occluded products of decomposition of the contaminating film, for it has been found that no transfer, or at most a very faint one, can be obtained from a chemically clean plate which has been flamed.

The results of the experiments on the electrical conductivity of flame tracks and of their transfers point to water molecules being one of the active substances, but the experiments with carbon monoxide and with sparks show that the effects cannot be attributed to water molecules alone.

The author has obtained some evidence that the transfer *in vacuo* of a breath figure to the sensitive surface of a photographic plate is capable of development, but the necessary conditions are as yet uncertain and require further investigation.

King Edward's School,
Birmingham,
Feb. 21, 1922.

LXVI *Repulsive Effect upon the Poles of the Electric Arc.*
By A. SELLERIO*.

1. **I**N December 1919 Prof. W. G. Duffield published the results of a careful series of experiments carried out in conjunction with Messrs. Burnham and Davis, on the same subject as the present paper †.

As similar experiments made by me are not mentioned there, it seems that my Note ‡ of 1916 is unknown to the authors. It may be useful to put together both the results concerning this interesting subject §: but before doing so, I must observe that in evaluating my readings I did not take account of the electromagnetic force V due to the earth's magnetic field, and of the electrodynamic action E between the fixed and the movable parts of the circuit. In recommencing my experiments some years ago, I remarked that V , E were on the contrary not to be neglected, and in the meantime I was notified of Prof. Duffield's work, in which the different sources of error are accurately separated. His investigation enables me to estimate the corrections concerning my results, without further trials.

* Communicated by the Author.

† Phil. Trans. Roy. Soc. of London, A, vol. ccxx. p. 109 (1919). A further note on metallic and composite arcs is recorded in Science Abs. 1920 (Roy. Soc. Proc. xvii. p. 326 (1920)).

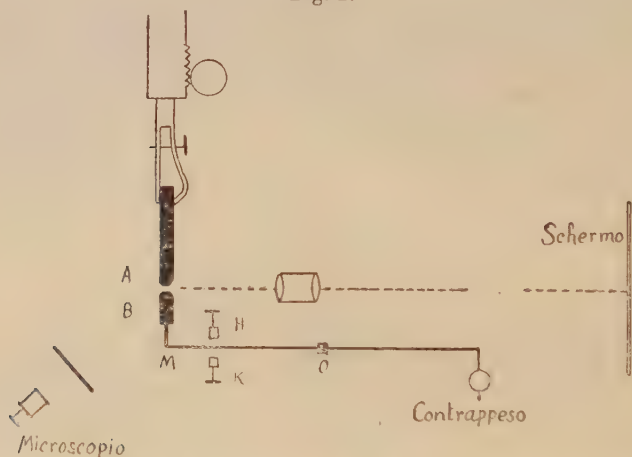
‡ A. Sellerio, "Effetto di repulsione nell' arco elettrico," *Nuovo Cimento*, xi. p. 67 (1916). This paper and the first noticed of Prof. Duffield will be denoted by the initials S. and D.

§ Duffield's research was the subject of a note by Mr. Ratner, Phil. Mag. xl. p. 511 (1920), and Prof. Tyndall, *ibidem*, p. 780.

It may be well to give an outline of my apparatus : a sort of torsion balance, shown in plan in fig. 1 (from the *Nuovo Cim.*).

At O were connected to the horizontal rod a suspension fibre normal to the plan hanging down from a graduated

Fig. 1.



torsion head, and a little iron style dipping into a mercury trough. Therefore the current flowed through the mercury either in the direction OMBA, or in the opposite one. Further details are referred to *loc. cit.*

When the arc is started, the arm OM tends to recoil, and to hold it stationary it is necessary to give to the fibre a certain torsion α , corresponding to a force

$$F = 0.036 \alpha \text{ dyne.}$$

In the force F there are to be distinguished :—

- The true repulsion rising within the arc gap ;
- Some disturbance occasioned from the heat, as air convection currents, etc. ;
- The influence V of the earth's magnetic field ;
- The electro-dynamic action E between OMB and the fixed circuit.

2. The earth's action V can be easily calculated, as follows :—

As the arm OMB is free to turn about a vertical axis, the recorded forces are only the horizontal one, and consequently the earth's field is acting upon OMB only with its horizontal

component, H_r . When B is +, the current direction is OMB, thus according with Fleming's law, the repulsion is apparently increased.

The resultant $H_r \cdot OM \cdot i$ of the forces acting on OM is applied to the centre of OM, hence on transferring it to the end M it is to be reduced to

$$H_r \cdot \frac{OM}{2} \cdot i.$$

In a similar way, the couple due to the forces acting on BM being $(H_r \cdot BM \cdot i) \cdot \frac{BM}{2}$, we may replace it with a force

$$(H_r \cdot BM \cdot i) \frac{BM}{2 \cdot OM}$$

applied to the extremity of the arm. As this force is much less than the preceding, when the length of the carbon rod BM during a set of experiments is reduced by burning, no appreciable error is caused.

Adding the two forces together, we have

$$V = H_r \cdot \frac{OM}{2} i + H_r \frac{BM^2}{2 \cdot OM} i,$$

or, by setting the current I in amp.,

$$V = \frac{H_r \cdot I}{20} \frac{OB^2}{OM}, \quad \dots \dots \dots (1)$$

This simple calculation of V may bring a remarkable economy in carrying out further experiments. Of course, it would be better to compensate both the actions V and E by some magnet or circuit conveniently disposed.

In my apparatus $OM = 15$ cm., $MB = \sim 4$ cm., $H_r = 0.37$ (Palermo), then

$$V = 0.296 I. \quad \dots \dots \dots (1')$$

Much more laborious and doubtful would it be to calculate E, *i.e.* the coefficient K of the law

$$E = KI^2, \quad \dots \dots \dots (2)$$

whenever the geometric data of the circuit were known. It is then preferable to estimate it experimentally, as Prof. Duffield did. He found (p. 124) with 8 amp. $E = 75$ degrees = 1.8 dyne, thus

$$K = 0.028,$$

$$E = 0.03 I^2. \quad \dots \dots \dots (2')$$

As my arrangement was a very similar one, I can adopt without committing (especially with small currents) a considerable error, the same value of E , and according to (1')-(2), the correction $(V+E)$ becomes

$$\left. \begin{array}{l} -0.296 I - 0.03 I^2 \dots\dots\dots \text{for the anode,} \\ +0.296 I - 0.03 I^2 \dots\dots\dots \text{for the cathode.} \end{array} \right\} \quad (3')$$

3. In my experiments almost all the readings were taken by keeping the arc length L constant and varying the current. But, having observed that the carbon quality has a far greater influence than L on the results *, it would be useless to relate here the individual series of measurements. In Table I. I have therefore recorded only the mean values of P upon anode and upon cathode for arc length $L=1\sim 4$ mm., by a given current, as they result from the whole of my readings after the corrections (3').

TABLE I.

Current amp.	ANODE.			CATHODE.		
	Deflexion α .	F dyne.	P_+ dyne.	Deflexion α .	F dyne.	P_- dyne.
3	36	1.30	0.14			
4	62	2.23	0.57			
5	88	3.16	0.93			
6	114	4.10	1.24			
7	140	5.04	1.49			
8	166	5.90	1.61			
9	204	7.35	2.26			
10	240	8.65	2.69			
11	290	10.4	3.49	16	0.58	0.29
12	336	12.1	4.23	48	1.73	0.96
13	380	13.7	4.77	80	2.87	1.66
14	436	15.7	5.68	112	4.03	2.31
15	480	17.3	6.07	144	5.19	2.87
16	540	19.4	6.97	176	6.35	3.38
17	600	21.6	7.88	210	7.55	3.87
18	260	9.35	4.95
19	318	11.50	6.35
20	376	13.60	7.42

4. Comparing Table I. with Duffield's results, we shall see, in spite of several numerical discrepancies, a good agreement in the general behaviour of the observed effect. So far as concerns the mean value $(\frac{1}{2}(P_+ + P_-))$, which is

* When the carbon rods are very close together ($L=\sim 0$), the repulsions P_+ and P_- become evidently greater.

independent of the earth's magnetic field, we shall find also a numeral concordance. For instance, by extrapolating for 11 amp. :—

From Duffield's Table VII. (Burnham),

$$L = 3.5 \text{ mm.}, \text{ anode } P = 1.55, \text{ cathode } P = 1.75,$$

$$\frac{1}{2}(P_+ + P_-) = 1.65 \text{ dyne};$$

From D.'s Table VII. (Davis),

$$\text{mean value } L = 2.5 \text{ mm.}, \text{ anode } P = 2.02, \text{ cath. } P = 1.78,$$

$$\frac{1}{2}(P_+ + P_-) = 1.90 \text{ dyne};$$

From Table I. (above),

$$\text{mean value } L = 2.5 \text{ mm.}, \text{ anode } P = 3.49, \text{ cath. } P = 0.29$$

$$\frac{1}{2}(P_+ + P_-) = 1.88 \text{ dyne.}$$

There is, on the contrary, a remarkable difference between the separated values P_+ and P_- , which may be due to the difficulty in eliminating V^* . The readings from Table VII., which are almost unaffected by V and E , show, according to my results, $P_+ > P_-$, *i. e.* a greater effect upon the anode.

5. In order to find out how other circumstances may influence the pressure P , I have tried some experiments with cored carbons, finding an increased effect upon the negative pole and a reduced one upon the positive. This behaviour is to be attributed to the metallic salts of the core (S., p. 77).

I have also noticed that the readings for *ascending* and for *descending* current are often a little different, as happens, for instance, in P. D. measurements, for both the shape and the matter of the carbon (occluding gases, metallic salts, grain, &c.) are altered by burning.

The diameter of the electrodes has no great influence in the present research, of course only while it remains large relatively to the crater size. For, putting a carbon rod 12 mm. in diameter against a similar one of 3 mm., when the latter is acting as anode, the arc hums and the repulsion becomes greater (S., fig. 8).

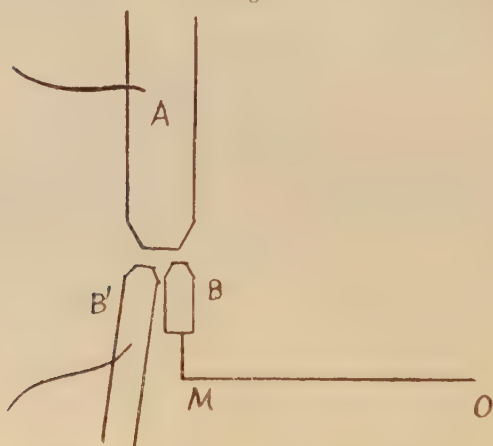
Further remarks, made also with thick carbon rods either

* In Duffield's experiments, setting approximately $H_v = 0.47$ (England) and taking $OM = OB = 11$ cm. from his figs. 1 and 17, formula (1) would give $V = 0.26$ I. Instead of 0.26, we get from fig. 8, 0.14, and from p. 124, 0.48.

by increasing the current strength over the hissing point, or by shortening the length L , &c., have generally shown that when the arc is not quite steady and silent, the forces acting upon the poles become greater.

6. In order to test whether the observed effect P is due to any disturbance C produced by heat, as convection currents of hot air, an arc was struck between two fixed carbon rods A , B (fig. 2, from the *Nuovo Cim.*). No repulsion was exerted upon a movable carbon B' , although it was so near to B as to become white hot. On the contrary, the influence of the heat is to cause the poles to approach each

Fig. 2.



other; the deflexion due to C was 10 to 20 degrees, or 0.36 to 0.72 dyne (S., p. 70). Then if we momentarily denote with O the observed effect, the true repulsion is to be set,

$$P = O + C.$$

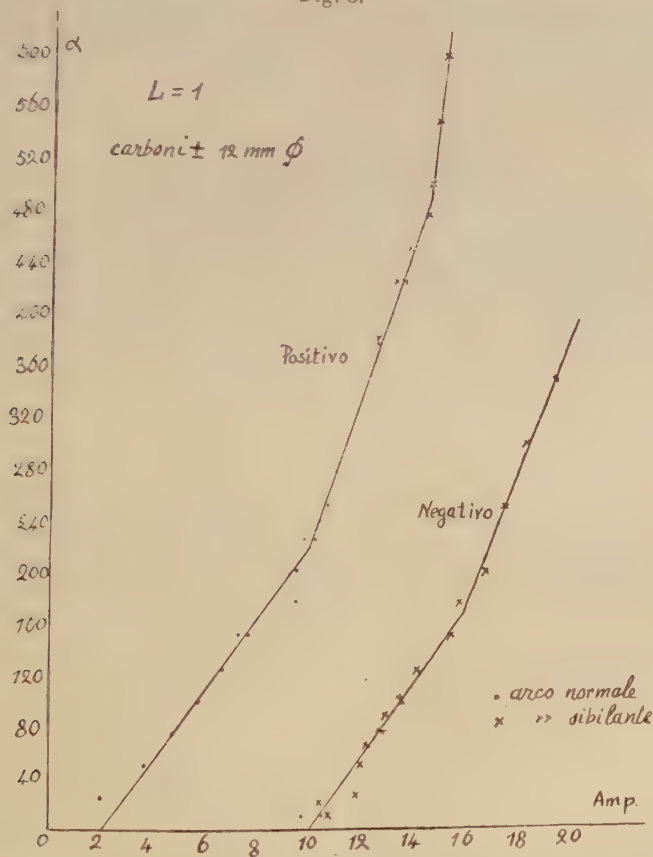
This disturbance is not entirely avoided by enclosing the apparatus in a box, to prevent air currents, as stated by Prof. Duffield. He tried to determine the value of C , and, having found approximately 0.44 dyne at 8 amp., proceeded to draw a correction curve C . However, "It is unfortunate that information is very difficult to obtain in the crucial part of the curve, where the current is small," as he says, thus we cannot yet decide with certainty whether the true repulsion P is present with the smallest currents, or whether it starts up only at a current *minimum*.

This interesting question is included in a general one,

i. e. either the repulsion P is a gradual and uniform effect, or not. Fig. 3 shows a typical specimen of my readings.

As the corrections V, E, C , whatever their exact values may be, do surely vary in the same way on increasing the

Fig. 3.



current, *i. e.* they as well as their derivatives are both continuous functions of I , the "Knees" remarked on graph 3 must remain after allowing for the corrections V, E, C , and consequently they are to be attributed to the true repulsion P .

If the explanation of P as a recoil effect by the departure of carbon ions or molecules is accepted, the different traits of the curves α or P are easily to be explained (S., p. 86) by assuming that when the current exceeds a certain value greater particles are also expelled from the craters.

7. The next point to be considered, as I pointed out *loc. cit.*, is the *specific pressure* $p = \frac{P}{A}$, that is, the pressure upon the unit surface of the crater, A being the whole area.

Taking from Duffield's fig. 22 the values P (as unaffected by E , V , and corrected for C), and, on the other hand, from my fig. 10 the values A for a circular crater normal to the carbon rod BM , we obtain

TABLE II.

1.	2.	4.	6.	8.	10.	amp.
Anode or } P	0.10	0.44	0.90	1.43	2.12	dyne
Cathode }						
Anode A	0.017	0.088	0.16	0.24	0.31	cm. ²
Cathode A .. .	0.005	0.027	0.050	0.073	0.096	>>
Anode p .. .	5.8	5.0	5.6	5.9	6.8	dyne/cm. ²
Cathode p ...	20	16.5	18	19.5	22	>>

This table shows that the unit force does not vary much with the current strength.

It must not be forgotten that, owing to the uncertainty in the data P , A , the above values are only recorded in order to give a rough estimate of the specific pressure p . To pursue accurately this inquiry, coherent values of P and A for the same carbons and the same arc length are required.

Besides the mechanical pressure, recent manometric observations with drilled carbons have shown for current strength under 20 amp. * a hydrostatic pressure up to 30 dyne/cm.², an order of magnitude not far away from that of the mechanical pressure p .

In a research † on the electric arc $Hg^+ C^{--}$ between Hg as anode and a thin carbon rod as cathode, I have calculated a pressure of 6500 dyne/cm.² upon the positive pole Hg . In fact, it is known that in a mercury arc a cavity of 1 mm. or more in depth has been often observed ‡, corresponding to a pressure range over 1300 dyne/cm.², with currents of a few amperes. With a carbon-carbon arc the specific pressure p is, as shown, a hundredfold smaller.

* H. E. G. Beer and A. M. Tyndall, *Phil. Mag.* xlii. p. 956 (1921).

† A. Sellerio, "Contributo allo studio quantitativo dell' arco elettrico fra mercurio e carbone," *Nuovo Cim.* xxiii. jan.-febr. 1922.

‡ Stark u. Reich. *Phys. Zeit.* iv. p. 323 (1902). See also, Stark u. Cassuto, *Phys. Zeit.* v. p. 269 (1904).

ON THE NATURE OF P.

8. For the purpose of explaining the observed mechanical pressure, many hypotheses have been suggested *, starting from different points of view on the arc mechanism, and a conscientious discussion would carry us beyond the limits of the present paper.

Without any assumption, it may be observed that of course in the arc a loss of matter by each electrode and a transport from anode to cathode occur, thus—on the anode at least—a recoiling effect must be occasioned. Whatever the nature of the forces propelling the carbon particles may be, the recoil due to evaporation can be estimated as follows :—

Let N, μ, v be respectively the number of particles leaving the crater in 1 second, their mass, and their *velocity of propulsion*; then the considered recoiling effect is given by

$$P = N\mu v. \quad (4)$$

By μ, v mean values are to be understood, for it is quite improbable that all the particles possess the same mass and are projected with uniform speed, therefore the right-hand side of (4) is a substitute for an expression $\sum n\mu v$, with $N = \sum n$.

In calculating the repulsion P as a recoil effect, by a formula similar to (4), Prof. Duffield assumes for v the velocity of agitation of carbon atoms at the temperature 4000°C. of boiling, that is,

$$18.39 \cdot 10^4 \sqrt{\frac{2}{12}} \sqrt{\frac{427.5}{273}} = 2.97 \cdot 10^5 \text{ cm./sec.,}$$

$18.39 \cdot 10^4$ being the molecular velocity of H_2 at 0°C. It seems to me that this assumption is hardly defensible, as will be best shown by means of the following analogy. If we keep a compressed gas in a bulb, by opening a tap the gas escapes, impressing a reaction upon the bulb, as in turbines. The velocity responsible for this recoil is not at all the molecular velocity of agitation (a function of the gas temperature), it is the velocity v with which the gas departs from the bulb (a function of the pressure difference in and out of the vessel). The value v will be obviously less than the molecular speed; thus the pressure P does not reach to the high range estimated by Duffield.

* Besides the works already noticed, see a recent paper of Prof. A. M. Tyndall, "On the Forces acting upon the Poles of the Electric Arc," Phil. Mag. xlii. p. 972 (Dec. 1921).

In my paper on the arc Hg^+/C^- , above mentioned, assuming for the vapours issuing from the anode the boiling temperature $357^\circ \text{C.} = 630 \text{ abs.}$, I have found a value $V = 1000 \text{ cm./sec.}$, whilst at the same temperature the atomic speed would be

$$18.39 \cdot 10^4 \sqrt{\frac{2}{200}} \sqrt{\frac{630}{273}} = 28,000 \text{ cm./sec.}$$

Even when the assumed temperature at the Hg crater is really higher, both the considered speeds remain too different from each other.

9. With a C/C arc, if the carbon consumption did occur only by evaporation in the crater, we should have, denoting with d the mean vapour density, a loss of mass per second,

$$m = A v d.$$

As, however, in an ordinary arc the carbon out of the crater is consumed also by burning in the air, we must write

$$m \geq A v d,$$

whence

$$v \leq \frac{m}{A d}. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

With reference to some of Duffield's researches*, we can take for the anode with $i = 8 \text{ amp.}$ and $L = 3 \text{ mm.}$, $m = 135 \cdot 10^{-5} \text{ g./sec.}$, the area A being 0.24 cm.^2 , as shown in Table II. The density of the carbon vapours at 4000°C. , being taken as 0.00009 , the abs. density of H_2 at 0°C. , becomes

$$d = \frac{12}{2} \frac{0.00009}{1 + \frac{4000}{273}} = 3.45 \cdot 10^{-5},$$

then we have from (5)

$$v \leq 650 \text{ cm./sec.},$$

a velocity range far removed from the atomic speed $2.97 \cdot 10^5$ mentioned above.

We will calculate in a simple manner what should be the average velocity v , so as to give account of the observed effect P.

* "Consumption of Carbon in the Electric Arc," Roy. Soc. Proc. A, vol. xcii, p. 122 (1915). Above data are taken from a "Note upon the Alternating-Current Carbon Arc," by Prof. Duffield and Mary D. Walker, Phil. Mag. vol. xl, p. 781 (1920).

If we momentarily assume as known the net carbon consumption m , *i.e.* the loss occurring by evaporation at the crater surface in 1 second, we can write instead of (5), the equation

$$\overline{m} = \text{Ave.}$$

It follows from (4), with $\bar{m} = N\mu$,

$$P = A \cdot v^2 \cdot d,$$

or for unit surface

$$P' = \frac{P}{A} = v^2 \cdot d,$$

$$v = \sqrt{\frac{p}{d}} \dots \dots \dots (8)$$

Taking p from Table II., we get a mean value

$$V = 400 \text{ cm./sec.}$$

in a good agreement with the foregoing upper limit 650.

If the observed p is half due to recoil and half to impact of particles moving towards the electrode, v becomes still less, *i. e.* 280 cm./sec. The values 400 or 280 mean that if $\frac{400}{650}$, *i. e.* 60 per cent., or $\frac{280}{650}$, *i. e.* 43 per cent. of the carbon waste occurs in the arc gap by evaporation, the calculated pressure agrees with the observed.

10. Hitherto we have made no hypotheses on the electrical nature of the particles issuing from the crater. It may be pointed out that the repulsion P, owing to the intensive evaporation due to heat, may be also produced from neutral carbon particles carrying no current, a trivial phenomenon.

If we assume, on the contrary, that the particles possess an electrical charge, and that the arc mechanism may be in the first instance reduced to a stream of positive ions of mean charge e moving from anode to cathode and carrying a current portion, aI , and to an inverse stream of negative ions (or electrons) carrying the rest $(1-a) \cdot I$, a system of equations may be written*, from which it follows

$$\frac{\epsilon}{\mu} = v_P \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot (9)$$

* S., p. 85. To correct $b_1 W_1 = \frac{1}{2} N_1 \mu_1 v_1^2 = b_1 a_1 \cdot \text{IE}$. According to Thomson ('Conduction' . . . p. 426 (1903)) the ratios $a, (1-a)$ should be proportional to the mobilities of the positive and negative carriers.

the cathode (S.). The range of p_+ and p_- is about 10 dyne/cm.².

4. It is yet not certain whether the law connecting P with I is a linear one, and whether the pressure does arise with every current strength (D.), or requires a current *minimum* (S.). Probably with increasing I, the pressure P does not increase by a uniform law, for the graphs show some "*knees*", which suggest different arc stages (S.).

5. The value P calculated, in testing the recoil hypothesis, by taking for the velocity of the carbon particles their atomic speed, is too great (D.). Whilst, by taking the *propulsion* velocity of carbon atoms starting from the positive crater, the calculated repulsion is in a far better agreement with the experimental results (S.).

6. The propulsive velocity of carbon particles has been estimated as 280–400 cm./sec. (S.).

In conclusion, I think we cannot yet say with full knowledge whether the observed effect is intimately associated with the electrical processes of the arc, or whether it simply accompanies in an ordinary way the evaporation of electrodes at high temperature. Only after having established the former view by further investigations, available information on the nature of the arc will be given by P measurements, improving the theoretical construction whose foundations have been established by Thomson, and Stark.

Istituto fisico della R. Università,
Palermo, 22 March, 1922.

LXVII. *The Path of an Electron in the Neighbourhood of an Atom.* By BEVAN B. BAKER, M.A., B.Sc., F.R.S.E.,
Lecturer in Mathematics in the University of Edinburgh *.

1. **E**XPERIMENT has shown that when an electron collides with an atom, thereby causing it to emit radiation, the frequency ν of the radiation is related to the amount U of the kinetic energy of the electron absorbed by the atom by the equation

$$U = h\nu,$$

where h denotes Planck's constant of Action. Professor Whittaker† has recently shown that, in order that all

* Communicated by the Author.

† E. T. Whittaker, "On the Quantum Mechanism in the Atom," Proc. Roy. Soc. Edin. xlii. pp. 130–142 (1922).

exchanges between the kinetic energy of the electron and the radiant energy should conform to this relation, it is necessary that the atom should contain a mechanism which is such that an electron approaching an atom will induce in the atom what may be called a "magnetic current"; the model which he has suggested to typify such a structure consists of a number of elementary bar magnets lying in a plane and rigidly connected like the spokes of a wheel, so that they rotate together in the plane, each magnet having one pole at the centre of the wheel and having its direction at every instant radial from the centre: it is, in fact, such a structure as Sir Alfred Ewing has proposed to explain induced magnetism*.

If we suppose such a magnetic wheel to be placed with its centre at the origin and its plane in the plane of yz , and suppose an electron to be projected towards it along the axis of x , then the electron, by its motion, creates a magnetic field which will cause the magnetic wheel to rotate, and the rotation of the magnetic wheel will set up an electric field which will retard the motion of the electron. Denoting the radius of the magnetic wheel by a , the magnetic moment of one of the elementary bar magnets by μa , the sum of the values of μ for all the elementary bar magnets composing the wheel by M , the moment of inertia of the wheel about its axis by A , the charge on the electron and the mass of the electron by e and m respectively, then Whittaker has shown that if the velocity of projection u_0 of the electron is less than $\frac{2eM}{\sqrt{Am}}$ the collision between the electron and the wheel is in the nature of an elastic impact, *i. e.*, the electron is stopped at a certain point and forced to return along its path, the magnetic structure giving back to the electron the energy it had previously received from it; but that if $u_0 \geq \frac{2eM}{\sqrt{Am}}$, the electron is able to pass completely through and away from the magnetic structure so as to be free from its influence, and the magnetic structure is left in rotation. In this latter case, the amount of energy U lost by the electron and gained by the wheel, is given by the equation

$$U = \frac{2e^2 M^2}{A},$$

and the absorbed energy appears in the atom as a magnetic

* Cf. Ewing, "On Models of Ferromagnetic Induction," Proc. Roy. Soc. Edin. xlii. pp. 97-128 (1922).

current, specified by the angular velocity $\Omega = \frac{2eM}{A}$, so that the absorbed energy and the angular velocity are connected by the equation

$$U = eM\Omega.$$

Whittaker has further shown that the disturbance in the atom after the collision consists in the displacement of a single electron, and that the radiation emitted by the electron in its oscillatory subsidence to its normal state must satisfy the equation $\dot{U} = h\nu$.

2. In his paper Whittaker has assumed that the electron is projected towards the magnetic wheel* in a line perpendicular to its plane and directly towards its centre. If we suppose the atoms to contain such structures as have been described, we must suppose the magnetic wheels in the substance to be bombarded to have all possible orientations, and the electrons to be projected from any direction. It is therefore of interest and importance to discuss the general case, when the electron is projected in any direction and passes in the neighbourhood of one of these magnetic wheels.

We will suppose, as before, that the magnetic wheel has a radius a , and that if μ is the magnetic moment of one of the elementary magnets, the sum of the quantities μ for all the magnets forming the wheel is M . Further suppose that the plane of the wheel is the plane of yz and that the wheel is free to rotate about its axis, which is the axis of x ; the wheel is therefore restricted to have only one degree of freedom. Let the amount of rotation of the wheel at any particular instant be specified by the angle ψ between the axis of y and a definite fixed radius in the plane of the wheel, the angle being considered positive when it is such as would turn the axis of y towards the axis of z , the rectangular axes of xyz forming a right-handed system. Let the moment of inertia of the wheel about its axis be A , so that when the wheel is rotating with angular velocity $\dot{\psi}$ its kinetic energy is $\frac{1}{2}A\dot{\psi}^2$. Let the mass of the electron be m , its charge e , and let its position at any instant be specified by spherical polar coordinates (r, θ, ϕ) connected with the rectangular

* *Note.*—When referring here or elsewhere to a magnetic wheel, it is to be understood that it is not suggested that an atom actually contains a mechanism similar to that here described, but merely that the atom behaves as if it contained such a structure.

coordinates (x, y, z) by the relations

$$x = r \cos \theta, \quad y = r \sin \theta \cos \phi, \quad z = r \sin \theta \sin \phi;$$

the kinetic energy of the moving electron is therefore

$$\frac{1}{2}m(\dot{r}^2 + r^2\dot{\theta}^2 + r^2 \sin^2 \theta \dot{\phi}^2).$$

We have further to determine the potential energy of the system due to the mutual interaction between the electron and the magnetic wheel. To do this the magnetic wheel, when it is rotating with angular velocity $\dot{\psi}$, may be looked upon as a magnetic current of strength $\frac{M\dot{\psi}}{2\pi}$ flowing in a circle of radius a . Now just as an electric current flowing round a circuit may be replaced by an equivalent magnetic shell bounded by the circuit, whose magnetic moment per unit area is proportional to the current-strength, so we may replace the magnetic current by an electric shell, bounded by the circuit, such an electric shell being equivalent to a charged condenser in electrostatics. For convenience we shall suppose the electric shell to have the form of a hemisphere of radius a bounded by the circumference of the magnetic wheel, the charge per unit area on either plate of the condenser being $\frac{M\dot{\psi}}{2\pi}$. The electric potential at any point P due to the condenser is therefore $\frac{M\dot{\psi}}{2\pi} \cdot \omega$, where ω is the solid angle subtended by the magnetic wheel at the point P. The potential energy V of the system is thus $\frac{M\dot{\psi}e\omega}{2\pi}$; it is independent of the coordinate ϕ , and may be expanded in powers of r in the form :

$$V = M\dot{\psi}e \left[1 - \frac{r}{a} P_1(\cos \theta) + \frac{1}{2} \frac{r^3}{a^3} P_3(\cos \theta) - \dots \right. \\ \left. \dots + (-1)^{n+1} \frac{1 \cdot 3 \dots (2n-1)}{2 \cdot 4 \dots 2n} \left(\frac{r}{a} \right)^{2n+1} P_{2n+1}(\cos \theta) + \dots \right]; \quad (1)$$

when $r > a$,

$$V = M\dot{\psi}e \left[\frac{1}{2} \frac{a^2}{r^2} P_1(\cos \theta) - \frac{1}{2} \frac{3}{4} \frac{a^4}{r^4} P_3(\cos \theta) + \dots \right. \\ \left. + \frac{(-1)^{n+1} 1 \cdot 3 \dots (2n-1)}{2 \cdot 4 \dots 2n} \frac{a^{2n}}{r^{2n}} P_{2n-1}(\cos \theta) + \dots \right]. \quad (2)$$

We shall write $V = M\dot{\psi}eF(r, \theta)$, where $F(r, \theta)$ is a function of r and θ alone, and $F(r, \theta) = \frac{\omega}{2\pi}$, where ω is the solid angle subtended by the magnetic wheel at the point (r, θ) .

The Lagrangian function $L = T - V$, where T and V are the kinetic and potential energies of the system respectively, is given by the equation

$$L = \frac{1}{2}A\dot{\psi}^2 + \frac{1}{2}m(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\sin^2\theta\dot{\phi}^2) - Me\dot{\psi}F(r, \theta). \quad (3)$$

The equations of motion of the system are therefore

$$A\ddot{\psi} - Me\left(\frac{\partial F}{\partial r} \cdot \dot{r} + \frac{\partial F}{\partial \theta} \cdot \dot{\theta}\right) = 0, \quad \dots \quad (4)$$

$$m(\ddot{r} - r\dot{\theta}^2 - r\sin^2\theta\dot{\phi}^2) + Me\dot{\psi}\frac{\partial F}{\partial r} = 0, \quad \dots \quad (5)$$

$$m(r\ddot{\theta} + 2\dot{r}\dot{\theta} - r^2\sin\theta\cos\theta\dot{\phi}^2) + Me\dot{\psi}\frac{\partial F}{\partial \theta} = 0, \quad \dots \quad (6)$$

$$m(r^2\sin^2\theta\ddot{\phi} + 2r\sin^2\theta\dot{r}\dot{\phi} + 2r^2\sin\theta\cos\theta\cdot\dot{\theta}\dot{\phi}) = 0. \quad (7)$$

3. If we multiply equations (4), (5), (6), and (7) by $\dot{\psi}$, \dot{r} , $\dot{\theta}$, and $\dot{\phi}$ respectively, add, and integrate we obtain

$$\frac{1}{2}A\dot{\psi}^2 + \frac{1}{2}m(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\sin^2\theta\dot{\phi}^2) = \text{constant},$$

which is the equation of conservation of energy of the system; if we suppose that initially the wheel is at rest and that the electron is projected from an infinite distance with velocity u_0 , the equation takes the form

$$\frac{1}{2}A\dot{\psi}^2 + \frac{1}{2}m\dot{r}^2 = \frac{1}{2}mu_0^2, \quad \dots \quad (8)$$

where r and $\dot{\psi}$ are respectively the velocity of the electron and the angular velocity of the wheel at any moment.

Moreover the coordinate ϕ is ignorable, the equation of motion corresponding to this coordinate being (7), which on integration gives

$$mr^2\sin^2\theta\cdot\dot{\phi} = \text{constant}; \quad \dots \quad (9)$$

this integral may be interpreted as the integral of angular momentum of the electron about the axis of the wheel. Equation (9) shows that if $\dot{\phi}$ is initially zero, it will remain so always, i. e., ϕ will have a constant value throughout the motion, as we should expect from the symmetry of the system. If, however initially, when r is infinite, $\dot{\phi}$ is not zero, and therefore necessarily $\sin\theta$ is not zero, we see that

the constant on the right-hand side of equation (9) is infinite, and since, from equation (8), $\dot{\phi}$ cannot become infinite, the value of r must remain infinite, or, in other words, the electron can never approach the neighbourhood of the magnetic wheel. To investigate the cases of interest we must therefore suppose ϕ to have a constant value which we can take to be zero without loss of generality, so that the motion of the electron is always in the plane of xy .

The equations of motion of the system then reduce to

$$A\ddot{\psi} - Me\left(\frac{\partial F}{\partial r} \cdot \dot{r} + \frac{\partial F}{\partial \theta} \cdot \dot{\theta}\right) = 0, \quad . \quad . \quad . \quad (10)$$

$$m(\ddot{r} - \dot{\theta}^2) + Me\dot{\psi} \frac{\partial F}{\partial r} = 0, \quad . \quad . \quad . \quad . \quad (11)$$

$$m(r\ddot{\theta} + 2r\dot{r}\dot{\theta}) + Me\dot{\psi} \frac{\partial F}{\partial \theta} = 0. \quad . \quad . \quad . \quad (12)$$

4. Equation (10) may be integrated immediately, giving

$$A\dot{\psi} - MeF(r, \theta) = \text{constant}. \quad . \quad . \quad . \quad (13)$$

Remembering that the wheel is initially at rest and replacing $F(r, \theta)$ by its value in terms of the solid angle subtended at the electron by the magnetic wheel, the value of $\dot{\psi}$, when the electron has reached any point P, is given by the equation

$$A\dot{\psi} = \frac{Me}{2\pi} \cdot \Delta\omega, \quad . \quad . \quad . \quad . \quad (14)$$

where $\Delta\omega$ denotes the increase in the solid angle subtended by the magnetic wheel at the electron, in its motion to P.

From equations (8) and (14) we see that when the electron moving with its initial velocity u_0 from a point at infinity, comes into the neighbourhood of the magnetic wheel, its velocity begins to diminish, whereas the wheel is set into rotation; the kinetic energy of the electron, in fact, is being expended in setting the wheel into rotation.

It may happen that the velocity and direction of projection of the electron are such that in its path it does not pass through the magnetic structure, *i. e.*, at no point of its path do we have $\theta = \frac{\pi}{2}$ or $\theta = \frac{3\pi}{2}$ and $r < a$ simultaneously; then in that case, when the electron has completed its path and passed again to an infinite distance, the total increment in the solid angle is zero and therefore, from equation (14), the magnetic wheel will come finally to rest: from equation (8) we see that the electron, in its later path, receives back

from the magnetic wheel the kinetic energy it had previously given up to it.

If, however, the direction and velocity of projection of the electron are such as to allow it to pass through the magnetic wheel, and, moreover, its energy is sufficient to allow it to pass away to infinity without returning through the magnetic structure, then the total increment in the solid angle will be 4π , and the magnetic wheel will be left in rotation with an angular velocity Ω , given by the equation

$$\Omega = \frac{2Me}{A} \quad \dots \dots \dots (15)$$

If u denotes the final velocity of the electron when it has passed again out of the influence of the magnetic wheel, we obtain from equation (8)

$$\frac{1}{2}A\Omega^2 = \frac{1}{2}m(u_0^2 - u^2) \quad \dots \dots \dots (16)$$

In this case the electron has given up to the magnetic structure an amount of kinetic energy U given by

$$U = \frac{1}{2}A\Omega^2,$$

or, using the value of Ω given by equation (15),

$$U = \frac{2M^2e^2}{A} \quad \dots \dots \dots (17)$$

From equations (15) and (16) we see that, in order that this should be possible, the initial velocity of projection of the electron must be at least as great as $\frac{2Me}{\sqrt{Am}}$, and, moreover, the direction of projection must be suitably adjusted.

5. The remaining possibility is that the electron should penetrate the magnetic structure but should not have sufficient energy to pass out of its influence. In this case the greatest value of $\dot{\psi}$ that can be attained by the wheel is given by

$$\dot{\psi}^2 = \frac{m}{A}u_0^2,$$

and therefore, from equation (14) the greatest value of $\Delta\omega$ is given by the equation

$$\Delta\omega = \frac{2\pi\sqrt{Am}}{Me} \cdot u_0 \quad \dots \dots \dots (18)$$

After attaining this value, the electron will return towards the magnetic wheel and must pass through it again in the

opposite direction, passing away again to infinity on the same side of the wheel from which it came originally, the previous motion being exactly reversed. From equations (8) and (14) it follows that, in the return path, the electron receives back from the magnetic structure the kinetic energy it had previously lent to it, and the magnetic wheel will return finally to rest.

The value of $\Delta\omega$ given by equation (18) is obtained on the assumption that the electron gives up to the magnetic structure all its kinetic energy; that this is so in general can be seen from the following considerations. When $\dot{\psi}$ has reached its maximum value, $\ddot{\psi}=0$, and therefore from equation (10)

$$\frac{\partial F}{\partial r} \cdot \dot{r} + \frac{\partial F}{\partial \theta} \cdot \dot{\theta} = 0. \quad (19)$$

From the expansions for $F(r, \theta)$ in powers of r given from equations (1) and (2) it is apparent that $\frac{\partial F}{\partial r}$ and $\frac{\partial F}{\partial \theta}$ cannot be simultaneously zero except when r is infinite: we have, in fact:

$$\left. \begin{aligned} &\text{when } r < a, \\ &\quad \frac{\partial F}{\partial r} = - \frac{1}{a} \cos \theta + \frac{3}{2} \frac{r^2}{a^3} (5 \cos^3 \theta - 3 \cos \theta) - \dots, \\ &\quad \frac{\partial F}{\partial \theta} = + \frac{r}{a} \sin \theta - \frac{1}{2} \frac{r^3}{a^3} (15 \cos^2 \theta - 3) \sin \theta + \dots; \\ &\text{when } r > a, \\ &\quad \frac{\partial F}{\partial r} = - \frac{a^2}{r^3} \cos \theta + \frac{3}{2} \frac{a^4}{r^5} (5 \cos^3 \theta - 3 \cos \theta) - \dots, \\ &\quad \frac{\partial F}{\partial \theta} = - \frac{1}{2} \frac{a^2}{r^3} \sin \theta + \frac{3}{8} \frac{a^4}{r^5} (15 \cos^2 \theta - 3) \sin \theta - \dots; \end{aligned} \right\} \quad (20)$$

and therefore, when $r \neq \infty$, $\frac{\partial F}{\partial r} = 0$ only when $\cos \theta = 0$, *i. e.*, when $\theta = \frac{\pi}{2}$ or $\theta = \frac{3\pi}{2}$ and $\frac{\partial F}{\partial \theta} = 0$ only when $\sin \theta = 0$, *i. e.*, when $\theta = 0$ or $\theta = \pi$.

In general, therefore, equation (19) will only be satisfied when $\dot{r} = 0$ and $\dot{\theta} = 0$ simultaneously, *i. e.*, when all the kinetic energy of the electron has been given up to the wheel.

There may, however, be certain exceptional values of r, θ , $\dot{r}, \dot{\theta}$ which will satisfy equation (19), even though the electron continues in motion: that even in these circumstances the electron will pass through the magnetic structure on its return path may be demonstrated thus.

Denote by α_r and α_θ the accelerations of the electron in the directions of r increasing and θ increasing respectively; then equations (11) and (12) may be written

$$\alpha_r = -\frac{Me}{m} \dot{\psi} \frac{\partial F}{\partial r}, \quad . \quad . \quad . \quad . \quad . \quad (21)$$

$$\alpha_\theta = -\frac{Me}{m} \dot{\psi} \frac{\partial F}{\partial \theta}; \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Suppose, for definiteness, that the electron is projected from a part of the plane of xy for which both x and y are positive; then $\dot{\psi}$ will be always positive and from equations (20), (21), and (22) we obtain the results:

when $r > a$ and $0 < \theta < \frac{\pi}{2}$; $\alpha_r > 0$ and $\alpha_\theta > 0$;

when $r > a$ and $\frac{\pi}{2} < \theta < \pi$; $\alpha_r < 0$ and $\alpha_\theta > 0$;

when $r > a$ and $\pi < \theta < \frac{3\pi}{2}$; $\alpha_r < 0$ and $\alpha_\theta < 0$;

when $r > a$ and $\frac{3\pi}{2} < \theta < 2\pi$; $\alpha_r > 0$ and $\alpha_\theta < 0$;

when $r < a$ and $0 < \theta < \frac{\pi}{2}$; $\alpha_r > 0$ and $\alpha_\theta < 0$;

when $r < a$ and $\frac{\pi}{2} < \theta < \pi$; $\alpha_r < 0$ and $\alpha_\theta < 0$;

when $r < a$ and $\pi < \theta < \frac{3\pi}{2}$; $\alpha_r < 0$ and $\alpha_\theta > 0$;

when $r < a$ and $\frac{3\pi}{2} < \theta < 2\pi$; $\alpha_r > 0$ and $\alpha_\theta > 0$.

The radial acceleration is therefore directed away from the centre of the magnetic wheel when x is positive, and towards the centre when x is negative, and thus always tends to retard the motion of the electron on its outward journey. Moreover, when x is positive and $r > a$ the curvature of the path is towards the axis of y ; when x is positive and $r < a$ the curvature is towards the axis of x ; when x is negative and $r < a$ the curvature is towards the axis of y ; and when

x is negative and $r > a$ the curvature of the path is towards the axis of x .

Now suppose that the electron has penetrated the magnetic structure and reached a point for which $r > a$ (if it only reaches a point for which $r < a$ it will obviously return through the magnetic structure); then in order that equation (19) should be satisfied we must have

$$\frac{\dot{r}}{r\dot{\theta}} = - \frac{\partial F}{r\partial\theta} \bigg/ \frac{\partial F}{\partial r} = - \frac{\alpha_{\theta}}{\alpha_r};$$

therefore, when $\frac{\pi}{2} < \theta < \pi$, \dot{r} and $r\dot{\theta}$ must have the same sign and when $\pi < \theta < \frac{3\pi}{2}$, \dot{r} and $r\dot{\theta}$ must have opposite signs; thus on the outward path, in both cases, the electron must at such a point be moving towards the axis of x , and so long as $r > a$ its motion will be such as to bring it to an even more favourable position for passing through the magnetic structure on the return journey.

6. It has therefore been shown that the electron can permanently transfer an amount of energy to the magnetic wheel only if its velocity and direction of projection are such that it penetrates the magnetic structure and passes away out of the influence of the wheel without returning on its path. In such a case the wheel is finally left in rotation with an angular velocity $\Omega = \frac{2Me}{A}$, and the amount of kinetic energy U transferred from the electron to the structure is given by $U = \frac{2M^2c^2}{A}$; in order to attain this result the initial velocity of the electron must be at least as great as $\frac{2Me}{\sqrt{Am}}$.

These results are precisely the same as those obtained by Whittaker in the particular case which he considered, and his further discussion of the way in which this absorbed energy is converted by the atom into radiant energy and the deduction of Planck's relation connecting the energy and the frequency of the emitted radiation may equally be applied in this more general case.

LXVIII. *On the Theory of Freezing Mixtures.* By ALFRED W. PORTER, D.Sc., F.R.S., F.Inst.P., and REGINALD E. GIBBS, B.Sc., A.Inst.P.*

IN 1874, Professor Guthrie carried out extensive experiments on freezing mixtures, and was the first to point out the fallacy of a belief which has persisted till even the present day. Guthrie said:—"In regard to freezing mixtures, I confess to have been here very much misled by the confident but rather erroneous statements of others, to which I attached faith trebly blind,—blind, because no recorded experiments really support them, blinder still because a little thought in the right direction must have shown their fallacy, and blindest of all because the one experiment of my own in this direction shows that the minimum temperature of an ice-salt cryogen is reached, whether we take the ratios three of salt to one of ice, or one of salt to two of ice, and so points to the wideness of the margin of ratios which may obtain between the weights of ice and the salt"†.

He showed that the same temperature, viz. the cryohydric, was reached for a wide range of proportions of the constituents, and that the initial temperature of the salt need not be zero; in fact, in his extreme case the salt was initially at a red heat.

The present object is to consider an equation representing the heat changes which occur in a freezing mixture, and to illustrate how well it bears out the truth of Guthrie's remarks.

For the sake of simplicity it is best to concentrate one's attention on a definite mixture, say that of salt and ice, and to suppose that initially the constituents are all at 0° C. and present in the following amounts: ice I gm., water \rightarrow zero, salt S gm. The vanishingly small quantity of water is introduced only to ensure that there will not be any discontinuity under the conditions which accompany the reaction. All possible cases can now be divided into three sections:—

- (1) That in which the masses of ice and salt are such that there are both free salt and free ice present at the end of the change of temperature.
- (2) That in which there is no salt remaining.
- (3) That in which there is no ice remaining.

* Communicated by the Authors.

† Proc. Phys. Soc. of London, vol. i. Jan. 18, 1875.

Case (1).

At the end of the change of temperature, let the mass of solution be $(M+m)$ gm., where

M = mass of water,

m = mass of salt in solution.

Since the solution is in equilibrium with the salt, it will be saturated, and as it is in equilibrium with ice, it will be at the freezing-point; hence the final temperature must be the cryohydric.

In determining the connexion between M and m at the end of the change, the external work done can be neglected owing to the very small change of volume at the moderate pressure of one atmosphere obtaining during the experiment. In these circumstances the *heat* change in a cycle can be taken as zero with sufficient approximation; or, in other words, the particular path of transformation is immaterial so far as heat changes are concerned. Representing the cryohydric temperature by $-\tau^\circ \text{C.}$, the heat equation will be

$$\tau(Is_i + Ss_s) = ML_w + mL_s,$$

where s_i and s_s are the specific heats of the ice and salt respectively, and where

L_w is the latent heat of fusion of ice at $-\tau^\circ \text{C.}$, and

L_s is the latent heat of solution of salt at $-\tau^\circ \text{C.}$

In writing this equation, all the salt and ice has been assumed to cool down initially to $-\tau^\circ \text{C.}$ and the transformation to take place then at this low temperature.

Nothing would be gained by aiming at meticulous accuracy in regard to numerical values. The general trend of results can be illustrated by using constant and approximate values for which the calculations can be made easily. As the solubility of salt varies very little with temperature, one can assume m/M to have a constant value $\frac{1}{3}$. Assuming also the following approximate values,

$$-\tau = -21.6^\circ \text{C.}, \quad s_i = .5, \quad s_s = .2,$$

$$L_w = 70, \quad L_s = 6 \text{ (at } -\tau^\circ \text{C.)}^*,$$

one obtains
$$m \doteq 1.0 \left(\frac{1}{2} + \frac{S}{5} \right).$$

* In calculating L_w at $-\tau$ the formula $\frac{\partial L_w}{\partial T} = 1 - s_i$ has been employed. It would even be erroneous to employ the more usual equation $\frac{\partial L_w}{\partial T} \cdot \frac{L_w}{T} = 1 - s_i$, because this gives strictly the latent heat under equilibrium conditions, *i. e.* under a pressure corresponding to a melting-point of $-\tau$, whereas the pressure is approximately atmospheric throughout.

Hence, if S is small, $\frac{S}{2}$ can be substituted for $\frac{S}{5}$,

whence
$$m \simeq \frac{I + S}{20},$$

and therefore
$$M \simeq \frac{3(I + S)}{20}.$$

This result is applicable, provided $S \ll \frac{I + S}{20}$.

On the other hand, if I is small compared with S , one obtains

$$m \simeq \frac{I + S}{50} \quad \text{and} \quad M \simeq \frac{3(I + S)}{50}.$$

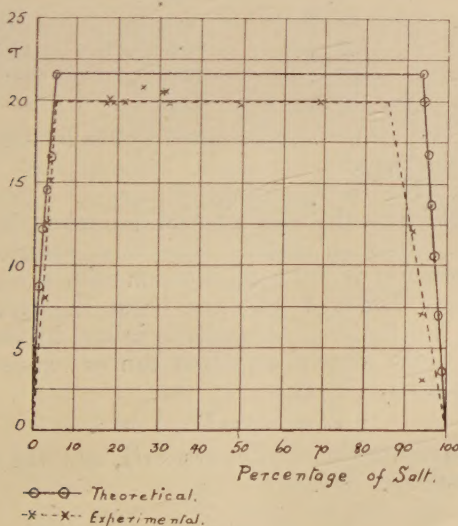
These results indicate that the cryohydric temperature will be attained, provided

$$(i.) \quad S \ll \frac{1}{20} (I + S)$$

$$\text{and} \quad (ii.) \quad I \ll \frac{3}{50} (I + S).$$

This is in agreement with ordinary experience, though the fact that they do not both totally disappear is usually attributed to the substances not having been taken in the

Fig. 1.



proper proportions. The above work, however, shows that no such "proper" proportion exists; and, in fact, the experimental results are of the kind one would expect according to theory.

In fig. 1 this range is represented by the central horizontal portion of the curve.

Case (2). No salt remaining.

As shown in the above equations, this means that in the original mixture, S is less than $\frac{1}{20}$ of the whole. The final temperature must be the freezing-point of the solution, as ice is in equilibrium with it, but it will not be the cryohydric temperature, as the solution is unsaturated (except in the limiting case).

The general equation can be adapted to this case by writing $m=S$;

$$\therefore \tau(I s_i + S s_s) = M L_w + S L_s.$$

The law connecting the freezing-point with the concentration, at least for dilute solutions, is $\tau = \frac{63S}{M+S}$.

The application of this law gives

$$\frac{63S}{M+S} (I s_i + S s_s) = M L_w + S L_s.$$

This has first to be solved for M, and then τ calculated from the previous equation. The values of τ for various values of I and S are shown in the following table:—

TABLE I.

S.	I.	M.	τ .
1 gm.	99 gm.	6.12 gm.	8.75° C.
2 "	98 "	8.4 "	12.1 "
3 "	97 "	10.0 "	14.6 "
4 "	96 "	11.2 "	16.5 "

In fig. 1 this range is represented by the left-hand sloping portion of the curve.

Case (3). No ice remaining.

This necessitates that the mass of ice taken is less than $\frac{3}{50}$ of the whole mixture. The final solution will be saturated because it is in equilibrium with the excess salt. On the other hand, it will not be at the freezing-point (except in the limiting case), as it is not in contact with ice. Again, the general equation can be adapted this time by writing $M=I$. Thus

$$\tau(I s_i + S s_s) = I L_w + m L_s.$$

The final concentration is of course m/I , and will be approximately one-third. Hence

$$\tau\left(\frac{I}{2} + \frac{S}{5}\right) = I\left(70 + \frac{1}{3} \cdot 6\right);$$

or approximately, as I is small,

$$\tau = \frac{360 I}{I+S}.$$

In fig. 1 this range is represented by the right-hand sloping portion of the curve, which is practically a straight line.

Series of experiments were carried out to test the validity of the above work. Not very much importance was attached to the absolute value of the cryohydric temperature reached all along the central portion of the curve, as this depended very largely on the purity of the materials used. One set of results is recorded below :—

Weight of Salt.	Weight of Ice.	Percentage of	
gm.	gm.	Salt $\frac{S}{I+S}$.	τ .
.80	27.6	2.82	8.0
.98	32.2	2.95	12.5
1.20	34.4	3.37	15.0
10.7	51.1	17.3	19.8
5.0	23.0	17.8	20.0
12.5	54.2	18.7	19.8
13.7	50.7	21.3	19.8
15.6	44.3	26.0	20.8
20.0	45.0	30.8	20.5
21.2	47.0	31.2	20.5
28.0	59.1	32.2	19.8
36.0	36.3	49.8	19.7
38.2	17.2	68.9	19.9
45.8	4.1	91.8	12.0
46.1	3.1	93.8	7.0
37.7	2.3	94.0	3.0

The above results were obtained by mixing the ice and salt in a small vacuum flask, great care being taken to make the mixing as complete as possible : this was fairly easy until the percentage of salt was high, say over 75 per cent. ; but for high percentages it was probably imperfect at best. The results agree with those expected from theory except for high concentrations of salt ; and, even for such, they are sufficiently close to substantiate the previous work. Poor mixing and the thermal capacity of the vessel would cause such a deviation.

In the practical case of the use of refrigerating mixtures, the body to be cooled is always to be taken into account, and it may produce considerable modification. If its thermal capacity is θ , the equation would now read

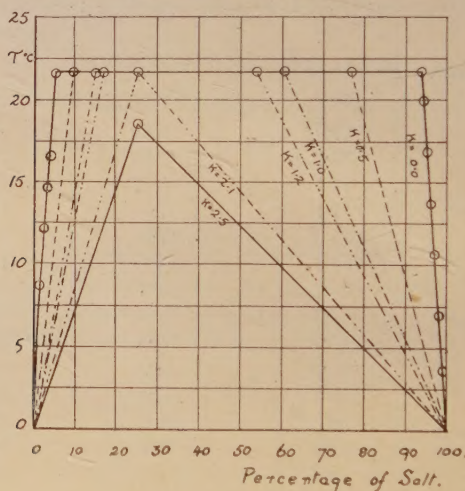
$$\tau \left[\frac{I}{2} + \frac{S}{5} + \theta \right] = ML_w + mL_s.$$

It is most convenient to write

$$\frac{\theta}{I+S} = K.$$

A few curves (fig. 2) have been drawn for different values of

Fig. 2.



K to show the effect produced. Possibly the most interesting case is to find the value of K for which the cryohydric is just reached. Assuming that all the salt and ice is used and that $m/M = \frac{1}{3}$, we have

$$21.6 \left[\frac{I}{2} + \frac{S}{5} + \theta \right] = 216m$$

$$\text{or} \quad \theta = 8.3S = 2.1(I+S),$$

$$\text{and hence} \quad K = 2.1;$$

therefore to cool a body whose thermal capacity is θ down to -21.6°C. , the quantities of materials to be used are $\theta/8.4$ gm. of salt and $\theta/2.8$ gm. of ice. In practice it is always necessary to take somewhat larger quantities to allow for the formation of dew on the exposed surfaces. This is a fairly serious factor, as 1 gm. of dew is equivalent in its heat change to roughly 8 gm. of ice. It will be seen, therefore, that if $K < 2.1$, there exists a central horizontal portion of the curve, whilst if $K > 2.1$, the two sloping lines intersect at a vertex lying on the 25 per cent. ordinate.